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16. Abstract

Bench scale batch experiments were performed on sludges obtained from lime neutralization of coal mine drainage in an attempt to alleviate present problems in sludge handling and disposal. Tests were of an exploratory nature and did not afford sufficient data for cost analyses. Ferro Magnetic sludge densification, filter aids, coagulant aids, heating, freeze drying, and coprecipitation of calcium carbonate through addition of CO_2 were tested. Of these, freeze drying, CO_2 addition, and ferro magnetic treatment were shown to be feasible alternatives to present disposal methods. Each of these methods resulted in settled sludge volume reductions of approximately 90% and increases in sludge solids contents of from 0.5 to about 5% after 30 min. settling periods. The ferro magnetic process has the advantages of possible recovery of a useful product, and elimination of costly settling lagoons, but is very sensitive to aluminum and requires a considerable amount of heat. Sludge freezing is the simplest conceptual approach and is apparently effective for any lime produced sludge. The CO_2 addition method offers the possibility of partial recovery and recycling of both CaO and CO_2 through sludge calcination. (Lowry-Texas)

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*Sludge disposal, *Dewatering, *Coal mine wastes, Sludge, Neutralization, Lime, Acid mine water, Freeze drying, Chemical precipitation, Filtration, Carbon dioxide, Coagulation, Sedimentation, Water quality control, *Waste water treatment

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*Magnetic precipitation

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Studies on Densification of Coal Mine Drainage Sludge

by

Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pennsylvania 15146

for the

ENVIRONMENTAL PROTECTION AGENCY

Project #14010 EJT

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ABSTRACT

The purpose of this research was to alleviate present problems in handling and disposal of sludges obtained by lime neutralization of coal mine drainage, through the investigation of various sludge densification techniques. The scope of the work was restricted to bench-scale batch experiments. Tests were largely of an exploratory nature and, as such, did not afford sufficient data to permit detailed cost comparisons among the various techniques.

In the first approach, conditions commonly employed in the lime treatment procedure (lime neutralization and aeration) were altered to produce a dense, fast-settling, ferromagnetic sludge. Although the properties of this sludge are sufficiently unique, the magnetic sludge conversion process includes a requirement for sludge heating and is quite sensitive to the presence of small amounts of aluminum in the original mine water.

In the second approach, recognized conditioning methods were applied to sludges obtained by the usual treatment procedure involving lime neutralization and aeration. These methods included the use of coagulant aids, sludge bulk additives (filter aids), seeding materials, and sludge heating and freezing.

In addition, exploratory tests were conducted on the introduction of carbon dioxide into the mine water to promote coprecipitation of calcium carbonate during lime addition.

Among the sludge densification methods tested, only three--magnetic sludge preparation, sludge freezing, and CO_2 pretreatment--appeared to be promising in terms of results obtained. Each method led to sludge volume reductions on the order of 90 percent and increases in sludge solids contents of from 0.5 to about 5 percent after 30-minute settling periods. Further developmental work would be desirable to determine the general usefulness and comparative costs of each method as applied to coal mine drainage treatment.

This report was submitted in fulfillment of Program No. 14010 EJT under the joint sponsorship of the Water Quality Office of the Environmental Protection Agency, the Commonwealth of Pennsylvania, and the coal industry through its research agency, Bituminous Coal Research, Inc.

Key Words: Coal mine drainage, sludge, sludge conditioning, magnetic sludge, iron removal, sludge densification, sludge disposal, stream pollution, pollution abatement, acid mine water treatment.

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SECTION I

CONCLUSIONS

Studies on coal mine drainage sludge densification have led to the following conclusions:

1. Coal mine waters containing iron principally in the ferrous (Fe^{2+}) state can be treated by a modification of the commonly practiced lime neutralization process to yield a ferromagnetic sludge. The sludge, presumably composed in large part of a hydrated ferrosoferric oxide ($Fe_3O_4 \cdot xH_2O$), is much denser and faster settling than the ordinary "yellowboy" sludge obtained by lime neutralization and aeration at ambient temperatures.

2. The magnetic sludge preparation technique involves (quantitative) precipitation of iron (largely as $Fe(OH)_2$) by the addition of hydrated lime to a pH of 8.5, separation of the resulting sludge from the aqueous phase, and heating of the sludge concentrate to at least 80 C (176 F), preferably higher, followed by mild aeration.

3. Magnesium, present as Mg^{2+} in most coal mine drainage waters, inhibits the formation of the magnetic sludge. This inhibition can be adequately minimized by keeping the pH below 9.6 during lime addition (thus avoiding the coprecipitation of $Mg(OH)_2$) and by separating the sludge from the bulk of the aqueous phase before the heating step, as indicated in (2) above.

4. Aluminum, commonly present in coal mine drainage waters, also inhibits the formation of the magnetic sludge. This inhibition is of practical significance when the molar ratio of aluminum/total iron is greater than 0.18. Below this value, sludges are still appreciably magnetic, but are bulkier and slower settling than those obtained when aluminum is absent. Unlike magnesium inhibition, aluminum inhibition cannot be minimized by the scheme indicated above, since aluminum precipitates as $Al(OH)_3$ near pH 4 and remains dispersed within the sludge.

5. The limitation on aluminum content is probably the most serious restriction affecting the feasibility of the magnetic sludge process as presently conceived. Nevertheless, a limited review of available water quality data has indicated that, in terms of relative acid and iron loadings, a significant number of major coal mine discharges in the eastern Ohio River basin may be amenable to treatment by a magnetic sludge process.

6. Data from tests on the use of magnetic seeding materials indicate that seeding did not enhance the formation of a magnetic sludge under the experimental conditions employed.

7. Based on the available experimental evidence, the magnetic sludge process appears to be technologically feasible. Preliminary cost considerations indicate that costs for sludge heating in the process would not be prohibitive.

8. The use of coagulant aids alone, of the anionic or nonionic polyelectrolyte types, will not result in an increase in the density of sludges obtained by lime neutralization of (synthetic) coal mine drainage. However, considerable increases in sludge settling rates and decreases in turbidity of the supernatant liquid are possible through the use of coagulant aids.

9. The use of filter aids or sludge "builders" such as fly ash, magnetite, "red dog," sand, blast furnace slag, sawdust, or gypsum can result in increased sludge densities and faster settling rates. The use of filter aids in combination with a coagulant aid appears to offer several advantages over the use of filter aids alone, such as faster settling rates, lower supernatant liquid turbidity, and a reduced coagulant aid requirement.

10. Among all the filter aids tested, only blast furnace slag and gypsum differed from the others in their proportionate ability to increase sludge solids contents as their concentrations increased. The blast furnace slag appears to offer certain added benefits as a sludge densifier. It is a relatively cheap waste product which also contains a reactive alkaline component, thereby reducing the lime requirement during neutralization of the mine water.

11. Filtration tests failed to show any dramatic improvements in sludge dewaterability when the filter aids were added as a "body feed." However, differences in behavior among the various materials evaluated, as well as effects due to filter aid concentration, indicate that some of the cheaper, more readily available materials might be successfully employed in a sludge densifying/dewatering application.

12. Tests involving the use of anhydrous ferric oxide, as well as freeze-dewatered and ordinary dried sludges (obtained by lime neutralization of synthetic coal mine water) as seeding materials failed to show any strong dependency of sludge properties on either the size of the seed crystals or the stirring rate employed, within the ranges 50 to 325 mesh and 300 to 480 rpm, respectively. The mere presence of the seed material was sufficient to promote increases in sludge densities and settling rates, and these effects became increasingly apparent as larger amounts of seed material were added to the suspension. However, these benefits in sludge properties were counteracted by a marked increase in the turbidity of the more heavily seeded samples after sludge settling. In all respects, the results of tests with seeding materials were quite similar to those obtained during the filter aid studies, and it is believed that whatever mechanism is involved in effecting sludge densification through the use of seeding materials,

it is probably not the usual mechanism involving growth of an ordered crystalline lattice on the seed crystal nuclei.

13. Attempts to effect densification of a synthetic coal mine water sludge by either heating the mine water before lime addition, or heating the concentrated sludge itself, were unsuccessful under the conditions employed (temperature range of 40 to 80 C, at atmospheric pressure.) Slight increases in sludge density were apparent when the sludge was allowed to settle immediately after heating. However, these increases were negated if the sludge was resuspended after cooling to room temperature, indicating that sludge dehydration by heating is a reversible process within the temperature limits employed.

14. In contrast to the results of sludge heating experiments, the effects of sludge freezing were rather striking, and significant increases in sludge density were observed after the frozen sludge had been thawed.

15. Dissolved CO_2 in coal mine waters, whether occurring naturally or added intentionally by CO_2 sparging, results in the coprecipitation of calcium carbonate during lime neutralization. This in turn results in a significant densifying effect on the sludge in terms of reduced sludge volumes and increased sludge solids contents. The effluents from lime treatment of mine waters containing appreciable amounts of dissolved CO_2 tend to be much more turbid than those in which CO_2 is essentially absent. This problem can be easily overcome through the use of coagulant aids, without any apparent attenuation of the sludge densifying effect.

16. Of all the approaches to sludge densification explored, three appear potentially promising in terms of the results obtained. These are magnetic sludge preparation, sludge freezing, and pretreatment of the mine water with carbon dioxide to effect coprecipitation of calcium carbonate during lime addition. Each of these methods resulted in settled sludge volume reductions of approximately 90 percent and increases in sludge solids contents of from 0.5 to about 5 percent after 30-minute settling periods. The magnetic sludge process has the advantage of possible recovery of a useful product. Sludge freezing is conceptually the simplest approach, and is apparently effective for any type of sludge resulting from lime treatment. The CO_2-addition method offers the possibility of partial recovery and recycling of the reagents (both CaO and CO_2) through sludge calcination.

SECTION II

RECOMMENDATIONS

The following additional studies are recommended:

1. Future development of the magnetic sludge process should involve optimization of the process variables; these include stirring rate, sludge heating time, aeration rate, method of preliminary sludge dewatering, and the effects of magnetic separation for final sludge processing. In addition, the matter of amenability of coal mine waters to treatment should be considered more thoroughly by means of a more comprehensive literature review as well as actual tests on mine drainage samples.

2. The technique of sludge freezing should be explored further. Emphasis should be given to conservation of energy in the process, and the filtration characteristics of the resulting sludges should be evaluated.

3. Further studies should be conducted on the feasibility of the CO_2-addition approach to mine drainage sludge densification. The filtration characteristics of product sludges should be evaluated, and the possibility of recovering and recycling the residual alkalinity of the sludge, either directly as $CaCO_3$ or as CaO plus CO_2 after calcination, should also be explored further.

4. Efforts should be made to develop cost data for the conceptual processes involving magnetic sludge formation, sludge freezing, and CO_2 pretreatment, with the purpose of selecting at least one of these processes for further testing at a field site.

5. The use of inexpensive waste materials (e.g. fly ash, "red dog," slag) as sludge additives, possibly in conjunction with coagulant aids, should be considered further. Results of the present studies have indicated that such materials, employed in relatively large amounts, increase the density and enhance the filterability of sludges from lime neutralization of coal mine drainage. The use of pulverized blast furnace slag in this regard appears particularly promising, and studies should be made to ascertain its availability, relative cost, residual alkalinity, and behavior as an additive in conventional mine drainage treatment processes involving lime neutralization and aeration.

SECTION III

INTRODUCTION

This is the final report on Project CR-102 under the auspices of the Department of Environmental Resources, Commonwealth of Pennsylvania.[1] The project was activated on January 5, 1970, with financial support from Bituminous Coal Research, Inc., the Pennsylvania Coal Research Board, and the Water Quality Office of the Environmental Protection Agency (WQO-EPA)[2] through Grant 14010 EJT to the Commonwealth of Pennsylvania. Work on the project was conducted according to the procedures outlined in BCR Research Program Proposal RPP-164R, dated April 24, 1969, and a subsequent Revision of Scope, dated February 25, 1970. This report covers the entire project period from January 5, 1970, through March 25, 1971.

Nature of the Problem

Most lime neutralization processes presently employed for the treatment of coal mine drainage yield a valueless, flocculent, gelatinous sludge which is slow-settling and difficult to dewater. The problem of handling and disposing of this sludge has been considered by some workers to be the greatest single obstacle associated with coal mine drainage treatment operations. Moreover, as the number of treatment plants continues to increase, increasingly larger volumes of sludge are produced, further aggravating the problem.

Objectives and Scope of the Research

The major objective of this research was to alleviate present sludge handling and disposal problems through the development of densification techniques for coal mine drainage sludge.

The work was divided into two broad areas. The first involved an approach whereby the usual conditions prevailing in the lime neutralization technique were altered so as to produce a dense, magnetic sludge. These studies were based on exploratory work (1)[3] conducted under an earlier BCR research program.

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[1] Formerly under the auspices of the Pennsylvania Coal Research Board.

[2] Formerly the Federal Water Quality Administration, Department of the Interior.

[3] Numbers in parentheses indicate references given in Section 7.

During these earlier studies it was found that dense, black or dark brown magnetic sludges could be obtained from both synthetic and natural mine waters by partial oxidation of ferrous hydroxide (precipitated by neutralization with hydrated lime) under controlled conditions of pH and temperature. Unfortunately, however, this conversion of ferrous hydroxide to a magnetic form is hindered by relatively small amounts of several other species common to most coal mine waters. Other workers have shown that magnesium (2, 3, 4) and aluminum (2, 5) inhibit the formation of magnetite in aqueous suspension. This inhibition is reportedly confined to pH ranges in which these ions exist as insoluble hydroxides, namely pH 4.1 to 10.8 for aluminum and pH > 9.6 for magnesium.(2)

Available experimental evidence indicates that small amounts of these impurities can be tolerated during the magnetic sludge transformation. Thus, Stauffer and Lovell (5) report that the ferromagnetic properties of sludges obtained by mixing heated suspensions of $Fe(OH)_2$ and $Fe(OH)_3$ were strong up to an Al/Fe molar ratio of 0.085, intermediate when this ratio was 0.123, and essentially negligible above a molar ratio of 0.184. On a parts per million (ppm) basis, for each 100 ppm of iron present the aluminum concentrations corresponding to these molar ratios are 4.1, 5.9, and 8.9 ppm, respectively. In similar experiments, Kakabadse _et al._ (4) found that dense, black magnetic precipitates prepared in the absence of magnesium became dark brown and less magnetic as magnesium was introduced up to a Mg^{2+}/Fe^{2+} molar ratio of 1.0. Beyond this value, the precipitate was lighter in color, gelatinous, and nonmagnetic. This molar ratio corresponds to 43.5 ppm of Mg^{2+} per 100 ppm of Fe^{2+}.

The data of these other investigators provided useful guidelines regarding the feasibility of a coal mine drainage treatment process based on the concept of magnetic sludge formation. Nevertheless, it was felt that the development of any such conceptual process necessitated a more complete study of reaction variables, the effects of interfering species, and possible means by which these interferences could be alleviated. Studies of this nature were included in the scope of the program as proposed, as well as studies to define the types of natural coal mine waters (or mixtures thereof) which would be amenable to treatment by a process resulting in magnetic sludge recovery.

The second general area of investigation involved the application of sludge conditioning techniques to densify sludges obtained by ordinary lime neutralization of coal mine drainage. Several of these techniques have been tested in sewage treatment studies as a means of enhancing the dewaterability of the sludge, and a few have been adapted to actual in-plant operations. In the area of coal mine drainage sludge treatment, however, these techniques have received only cursory attention as indicated by the few scattered references in the pertinent literature.

Those techniques chosen for study in the present investigation included the use of coagulant aids, filter aids, seeding materials, sludge heating and freezing, and the use of dissolved carbon dioxide gas to promote the coprecipitation of calcium carbonate during lime neutralization. The relative effectiveness of each of these sludge conditioning techniques was judged on the basis of changes in sludge settling rate, settled sludge volume and solids content, and turbidity of the supernatant liquid after sludge settling. In addition, some limited tests on sludge filterability were conducted in conjunction with the filter aid studies.

The studies on magnetic sludge preparation and sludge conditioning were carried out according to the work schedule shown in Figure 1.

It should be noted that the scope of the program did not include an evaluation of the economic feasibility of these various sludge densification techniques as applied to the treatment of coal mine drainage sludge. However, this admittedly important aspect of the problem was considered in a qualitative manner in judging the potential usefulness of the various approaches, and pertinent remarks regarding cost factors are included throughout this report.

Activity	Month, 1970-1971														
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
A. Magnetic Sludge Studies															
1. Determination of Interference Tolerance Limits	■	■	■												
2. Adaptation to Mine Water Treatment				■	■	■	■								
3. Evaluation of Magnetic Sludge Properties	■	■	■	■	■	■	■								
B. Sludge Conditioning Studies															
1. Coagulation								■							
2. Filter Aids									■						
3. Seeding										■					
4. Heating and Freezing											■				
5. Miscellaneous Approaches												■	■		
C. Comparison of Results and Reporting														■	■

Bituminous Coal Research, Inc. 2038G18

Figure 1. Schedule of Work—Recovery of Iron in a More Dense Form from Coal Mine Drainage

SECTION IV

EXPERIMENTAL PROCEDURE

Materials, Equipment, and Analytical Techniques

Four actual coal mine waters were used in various phases of the research program. All were from the Sewickley Creek area in Westmoreland County, Pennsylvania. The BCR designations, site locations, and nature of the mine water samples are described briefly in the following paragraphs.

Keystone

An inactive drift mine in Sewickley Township located near the junction of Sewickley Creek with the Youghiogheny River, approximately 200 feet west of Pennsylvania 64104 and 0.5 mile south of the junction of this road with Pennsylvania T-400. Samples are characterized by a relatively high ferrous iron and sodium content and by a relatively high pH. The ferric iron present tends to hydrolyze and precipitate fairly readily during storage of the mine water.

Brinkerton

An inactive shaft mine in Mount Pleasant Township located on the south side of railroad tracks, 0.2 mile west of their junction with Pennsylvania T-778 and at a point 0.2 mile south of the junction of this road with Pennsylvania 64130. Except for lower iron (and sodium) concentrations, this water is quite similar to the Keystone discharge. Both Keystone and Brinkerton are relatively large-volume discharges, each of about 3,000 gpm.

South Greensburg

An inactive drift mine in Hempfield Township located on the north side of Pennsylvania T-681 northwest of its junction with Pennsylvania 64111. Samples are characterized by the usual absence of ferric iron and a fairly constant composition in spite of variations in flow rates.

Tarrs

An abandoned mine site in East Huntingdon Township about 0.5 mile southwest of the town of Tarrs, Pennsylvania. Samples contain relatively high concentrations of silicon and aluminum.

Mine water batch samples were collected in 5-gallon carboys and used in the experiments the same day.

Studies on sludge conditioning reported herein were conducted using a synthetic coal mine water. This synthetic mine water was prepared from directions furnished by Mr. R. D. Hill of the WQO-EPA, and is essentially a 0.01 N sulfuric acid solution containing specified amounts of the sulfate salts (chemical reagent grade) of iron, aluminum, magnesium, calcium, and manganese. The synthetic mine water was prepared as needed in 15-liter batches and stored in a 5-gallon polyethylene carboy.

Representative analytical data for the four actual coal mine waters as well as the WQO-EPA synthetic mine water are shown in Table 1. Values for the Fe^{2+}/total iron ratios indicate that all of these mine waters with the exception of the Tarrs discharge can be considered as "ferrous" waters.

Measurements of pH were accomplished using an Orion Model 401 Specific Ion Meter. A Sargent combination pH electrode was used for measurements at or near room temperature; pH measurements at elevated temperatures were accomplished with a Sargent high-temperature glass electrode and a reference electrode containing silver-silver chloride internals. When appropriate, changes in pH with time were recorded using a Houston Instrument Omnigraphic T-Y recorder, Model HR-80.

Experiments involving sludge heating were conducted with the aid of a Cole-Parmer Model 3431 hot plate regulated by an immersion probe for automatic temperature control.

A Hach Model 2100 Laboratory Turbidimeter was employed for turbidity measurements during the sludge conditioning studies. All turbidity values reported herein are in Jackson Turbidity Units (JTU).

Electrophoretic mobility measurements were accomplished using a Zeta-Meter (Zeta-Meter Inc., New York, New York).

X-ray diffraction analyses were conducted using a Picker x-ray generator with the powder camera technique.

Ferrous iron concentration was determined by the colorimetric method using ortho-phenanthroline. Sample absorbance was measured at 510 mμ using a Cary Model 14 spectrophotometer. Total iron as well as aluminum, magnesium, calcium, manganese, silicon, and sodium were determined by emission spectrographic analysis (solution technique) using a Jarrell-Ash Model 78-000 1.5-meter Wadsworth grating spectrograph.

"Hot" acidity was determined by titration of the sample with 0.1 N NaOH to pH 8.2. The sample was first treated with 5 drops of 30 percent H_2O_2 to oxidize all iron, heated to near boiling for four to five minutes, and cooled to room temperature. "Cold" acidity was determined in a similar manner except that the heating step in the procedure was omitted. All acidity values reported herein are expressed as ppm $CaCO_3$ equivalents, and unless indicated otherwise, all values are from "hot" acidity determinations.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF COAL MINE WATERS USED IN SLUDGE DENSIFICATION STUDIES

Source	pH	Spectrographic Analysis, ppm Fe	Al	Mg	Ca	Mn	Si	Na	Fe^{2+}/Total Fe Ratio
Keystone	6.2	255	< 2*	100	242	4	7	1,144	0.91
Brinkerton	5.7	131	< 2*	81	198	4	8	59	0.88
South Greensburg	4.9	110	8	85	210	4	12	80	0.91
Tarrs	3.1	95	48	84	204	4	40	< 50*	0.47
WQO-EPA Synthetic	2.2	200	15	24	80	8	--	--	1.00

* Below the limits of accuracy of the analytical technique

Magnetic Sludge Studies

Magnetic Sludge Factorial Experiment

The first phase of the research program involved a study of important variables affecting the formation of a magnetic sludge, particularly those relating to interferences caused by the presence of foreign cations such as Al^{3+} and Mg^{2+} in the system. Toward this end, a factorial experiment was designed to determine the effects of temperature, pH, Al/Fe ratio, Mg/Fe ratio, and interactions of these variables on the magnetic properties, settling rate, and volume of sludge produced during neutralization of a synthetic mine water with hydrated lime. The methodology involved in this factorial experiment was based on a recent publication on statistically designed experiments.(6) The experiment consisted of 16 tests; initial iron concentration (300 ppm), stirring rate (188 rpm), and aeration rate (50 cc/min) were held constant throughout the series of tests.

The experimental procedure was as follows: Aliquots of stock solutions of ferrous sulfate, aluminum sulfate, and magnesium sulfate were added to an 800-ml beaker and diluted to a total volume of 500 ml to obtain the desired Al/Fe and Mg/Fe molar ratios. Stirring was commenced and the solution was brought to the desired temperature (25 or 90 C). The pH was then adjusted to the desired value (8 or 10) by dropwise addition of a 10 percent w/w $Ca(OH)_2$ suspension and aeration was started. The pH of the suspension was maintained at the desired level during the test, and changes in color were noted. In addition, a small portion of the suspension was withdrawn early in the test and filtered; aliquots of the filtrate were analyzed for residual dissolved Fe^{2+}.

At the end of a 60-minute reaction period, the beaker was removed and solids were allowed to settle by gravity for one hour. The supernatant liquid was then decanted, and the sludge was transferred to a 100-ml graduated cylinder for measurement of settling rate. The volume of the suspension was made up to 110 ml, and timing was started when the sludge-liquid boundary passed the 100 ml mark of the cylinder. After 60 minutes, final settled sludge volume was recorded. The settling rate was determined by plotting the sludge volume versus time and calculating the slope of the linear portion of the settling rate curve. All values were converted to centimeters per minute based on the actual height of the graduated cylinder.

Magnetic response of the settled solids was checked qualitatively with a hand magnet, and if the sludge was magnetic, the solids were filtered in a 30-ml medium porosity fritted glass funnel with suction, washed several times with acetone, and dried at room temperature. The solids were then pulverized to a granular powder, and a small sample (0.20 g) was transferred to a tared 15-ml beaker. The beaker was placed on the pan of a modified Torbal torsion balance directly above a cylindrical pot magnet, which was 1-3/16 inches high and 1-3/8 inches in diameter.

The weight required to overcome the pull of the magnet, minus the tare weights of the beaker and sludge sample, was determined as a quantitative measure of magnetic response. Although this technique was admittedly crude compared to the usual methods for determining magnetic susceptibility, it was rapid and sufficiently reliable for our purposes. This is indicated further by the data in Figure 2, which show the magnetic response of various ferromagnetic materials measured by this technique as a function of sample weight. The materials tested included reagent grade iron powder, a synthetic magnetite (about 92 percent Fe_3O_4), a synthetic maghemite (essentially pure γ-Fe_2O_3), and two magnetic sludge samples prepared from Keystone mine drainage. Although the curves in Figure 2 tend to tail off with increasing sample weight, the data indicate that the relationship of magnetic response to sample weight is, as shown by the dashed lines, reasonably linear below a sample weight of about 0.40 g. In view of these results, it was felt that the procedure was suitable as a means of comparing magnetic properties of various materials on a relative basis, as long as sample weight did not exceed 0.40 g.

Effects of Magnesium and Aluminum Interference

The interference of magnesium and aluminum with magnetic sludge formation was studied using essentially the same experimental procedure as that described above for the factorial experiment. Initial experiments were conducted using synthetic coal mine waters containing appropriate aliquots of stock solutions of ferrous sulfate, magnesium sulfate, and/or aluminum sulfate diluted to a total volume of 500 ml. The initial iron concentration (300 ppm), stirring rate (188 rpm), and aeration rate (50 cc/min) were held constant during all experiments. Based on results from the earlier factorial experiment, it was decided that preferred reaction conditions were pH 8.0 and 90 C. Accordingly, magnetic sludge preparations were carried out under these conditions.

Originally, these tests involved heating the mine water sample to 90 C, adding hydrated lime slurry to attain a pH of 8.0, and aerating the suspension during a 60-minute reaction period. Later in the investigation, it was found that interference from magnesium could be minimized through a preliminary sludge concentration step in the procedure, and the experimental procedure was altered slightly as follows:

To a 6,000-ml batch sample of the synthetic or actual mine water, sufficient hydrated lime in the form of a 10 percent slurry was added to the sample with stirring to raise the pH to 8.5 and precipitate iron, primarily as $Fe(OH)_2$. The sludge was allowed to settle for a predetermined time period, after which the supernatant liquid was carefully removed by siphoning. During the sludge settling period a portion of the supernatant liquid was withdrawn, filtered, and analyzed for residual dissolved iron. In cases where centrifugation was employed, the sludge was first allowed to settle by gravity for one hour, then the settled sludge was dewatered as noted above and centrifuged in an

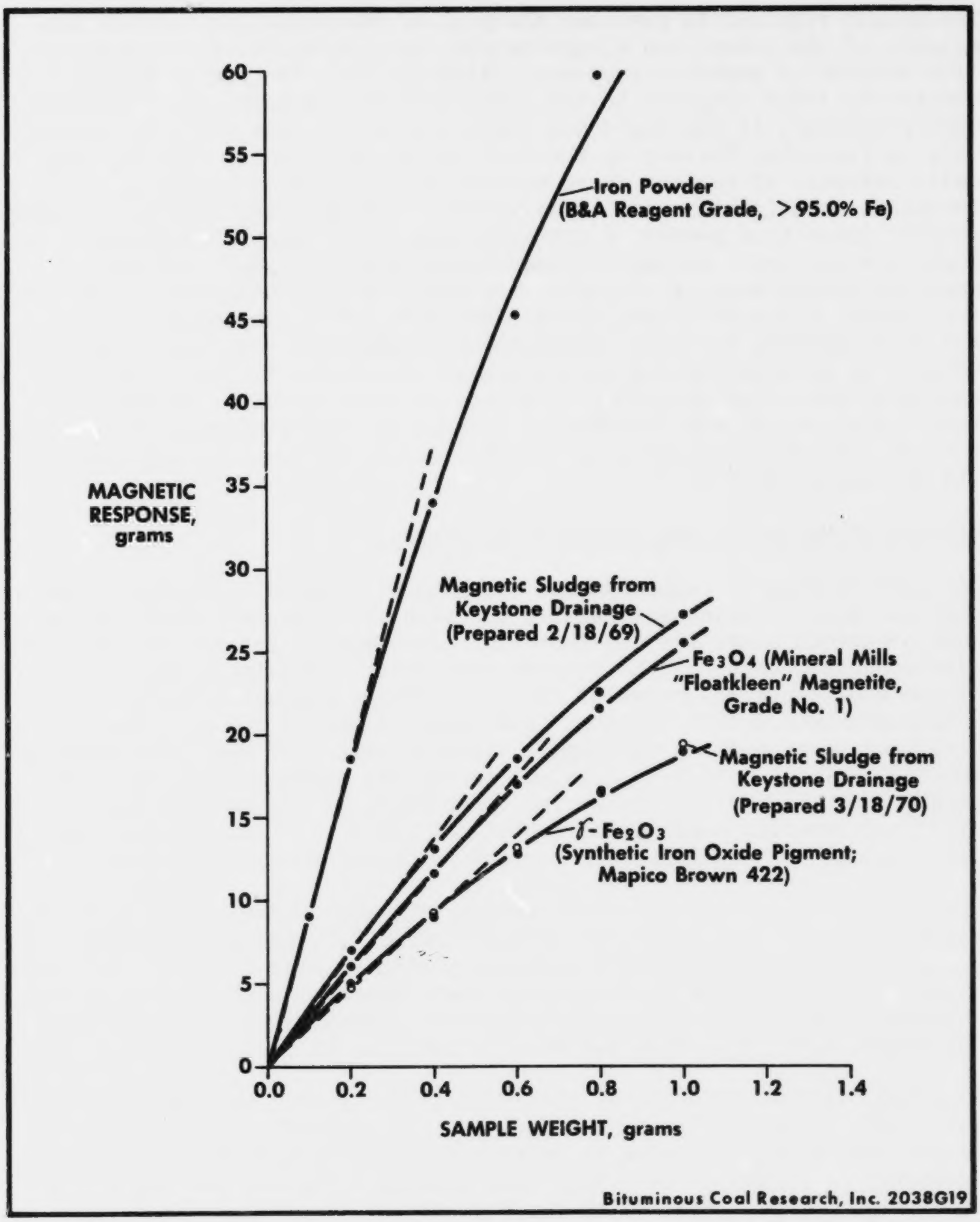

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Figure 2. Magnetic Response of Various Ferromagnetic Materials with Increasing Sample Weight

International Model V trunnion-head centrifuge (International Equipment Company, Boston, Massachusetts) for ten minutes at 1,500 rpm.

The volume of the gravity-concentrated (or centrifuged) sludge was measured, and a sample was taken for solids content determination. The bulk of the sludge was then converted to a magnetic form by heating at 90 C for 30 minutes with stirring and aeration. At the end of the heating period the magnetic sludge was transferred to a graduated cylinder, and settled sludge volume was recorded after one hour, after which the supernatant liquid was removed and a sample of the sludge was taken for solids content analysis once again. A portion of the magnetic sludge was filtered with suction, dried by acetone washing at room temperature, and pulverized by grinding with a glass rod. A 0.200 g sample of the dried sludge was used for magnetic response measurement. A second portion (about 70 mg) was dissolved in 5 ml of concentrated hydrochloric acid and the resulting solution was diluted to 100 ml in a volumetric flask. A 25-ml aliquot of this solution was then taken for the determination of Mg/Fe and Al/Fe molar ratios by emission spectrographic analysis.

The experiments on magnetic sludge seeding involved the earlier approach of preheating the mine water sample to 90 C. Weighed amounts of the seed material were added to the heated sample, just before lime addition (to pH 8.0) and aeration (for 60 minutes) were commenced. The seed material used in these tests was a magnetic sludge prepared from the Keystone mine water on March 18, 1970, as follows: Hydrated lime was added with stirring to 90 gal of the raw mine water until a pH of 8.5 was attained. No residual dissolved iron was detected at this pH. The sludge settled overnight to a volume of about 2.5 gal. The supernatant liquid was removed and the sludge concentrate was heated to 90 C and maintained at that temperature for one hour with stirring but no aeration. A dark brown, strongly magnetic sludge was obtained which settled overnight to a volume of 0.53 gal. A portion of the settled sludge was filtered on a Buchner funnel, dried at 107 C for two hours, ground to a fine powder, and sieved to a particle size fraction of 325 x 400 mesh for use in the magnetic sludge seeding tests. (This material was also used for magnetic response measurements, shown earlier by Figure 2. It is interesting that this magnetic sludge prepared from the Keystone discharge exhibits essentially the same response in a magnetic field as do commercially available ferromagnetic iron oxides.)

Sludge Conditioning Studies

Coagulant Aid Studies

For the coagulant aid addition studies, the following procedure was developed for sludge preparation. To a 1,000-ml sample of the WQO-EPA synthetic mine water, hydrated lime ($Ca(OH)_2$) was added as a dry powder with stirring. The amount of lime added was equivalent to the exact stoichiometric requirement based on the mine water total acidity.

Aeration was commenced at a rate of 2,500 cc/min, and aeration and stirring were continued during a 30-minute reaction period. Analyses for residual dissolved iron showed that complete iron oxidation and precipitation occurred within the 30-minute reaction period. The final pH of the sludge suspension was about 7.8.

Aliquots (100 ml) of the sludge suspension were transferred to 250-ml beakers and the desired amount of coagulant aid was added. The suspension was stirred for one minute at low speed, after which samples of the suspension were withdrawn for electrophoretic mobility measurement with the Zeta-Meter. Coagulant aids were prepared as 1,000 ppm stock solutions, and aliquots of these stock solutions were diluted as necessary to obtain the desired coagulant aid concentrations in the sludge suspensions.

For the determinations of settling rate and solids content, 100-ml aliquots of the synthetic mine water sludge suspension were taken and treated with selected amounts of coagulant aids as described above. The samples were then transferred to 100-ml graduated cylinders and the cylinders were stoppered and inverted three times. Sludge settling rates were measured and the settled sludge volume was recorded after a 30-minute period. Samples of the supernatant liquid were then withdrawn for turbidity measurements. Finally, the remainder of the supernatant liquid was drawn off by careful siphoning, and a sample of the wet sludge was taken for solids content determination. Sludge samples were dried in an oven at 105 C to constant weight.

Filter Aid Studies

In the studies on filter aid addition, the requisite amount of the selected filter aid was added to a 500-ml batch sample of the synthetic mine water with stirring. Changes in pH produced by the filter aids, if any, were monitored for a one-minute period, then hydrated lime was added to the suspension and aeration was commenced. In cases where the filter aid material effected an initial increase in pH, the amount of lime added was that fraction of the stoichiometric amount necessary to achieve a final pH of 7.8. After a 30-minute aeration period, 100-ml aliquots of the suspension were taken for electrophoretic mobility measurement and for determinations of settling rate, 30-minute settled sludge volume, solids content, and turbidity, by the procedures described earlier. In addition, the behavior of sludges containing the filter aids only was compared with that of the same sludges after treatment with a coagulant aid.

Filtration Tests

In conjunction with the filter aid studies, a series of batch filtration tests was conducted using a modified leaf test procedure.(7) The sludge suspension was prepared by adding the desired amount of filter aid to 1,000 ml of the synthetic mine water, followed by hydrated lime;

the mixture was then stirred and aerated for a 30-minute period, resulting in complete oxidation and precipitation of the iron. The amount of lime added was that sufficient to achieve a final pH of 7.8 in the sludge suspension.

The sludge sample was then transferred to a magnetic stirrer (except for those samples containing magnetite, in which case a small mechanical stirrer was employed) and the leaf filter was immersed about 2 inches below the surface. Stirring was commenced, and a vacuum of 18 inches of mercury was applied to the filter.

Filtration was carried out for a 10-minute period, then the filter was withdrawn from the suspension, mounted in a vertical position, and suction was continued for an additional 5-minute period to simulate a cake dewatering cycle. The filtrate volume was measured and the weight of the wet filter cake was recorded. The filter cake was then dried in a dessicator at room temperature to constant weight.

The filter used for the filtration tests consisted of a standard Millipore glass filter base connected by rubber vacuum tubing to a 1,000-ml filtration flask. Millipore membrane filters (MF type) of 8µ pore size were used throughout the tests, and were held to the filter base by two grooved Plexiglas rings connected by small springs. The filtration flask was also connected to a U-tube mercury manometer and was equipped with an air bleed valve to regulate vacuum, which was obtained using a Model 4K Neptune Dyna-Pump.

It was found difficult to effect a quantitative transfer of the small amounts of damp filter cake obtained (on the order of 400 mg) to a separate container for weighing. Consequently, the weight of wet sludge was determined by subtracting an average tare weight of the damp filter paper. Measurements made on six filter disks showed an average dry weight of 64.8 ± 1.3 mg and an average wet weight (after filtration cycles with deionized water alone) of 247.7 ± 9.6 mg. Only those filter disks whose initial dry weights were within the limits indicated were chosen for use in the filtration tests.

Seeding Experiments

The nature of the precipitate formed in the presence of seed crystals is known to be influenced to a large extent by seed crystal size, seed crystal amount, and agitation rate.(8) Accordingly, tests on the use of seeding materials were designed to consider the effects of these three variables, as well as the presence or absence of the seed material itself, on sludge properties. Most of the tests involved the use of anhydrous ferric oxide (Fisher Certified Reagent grade) which was obtained in the form of a red powder. The material was sieved to obtain the following particle size fractions (U.S. Sieve Series): 50 x 80 mesh (297 x 177µ, average 237µ), 100 x 140 mesh (149 x 105µ, average 127µ), and 200 x 325 mesh (74 x 44µ, average 59µ). Thus the average particle sizes for each fraction were in the ratio of 4:2:1, respectively.

In the tests on the effect of seed crystal size, the various particle size fractions of the seed material were added to 1,000 ml of the synthetic mine water to a concentration of 100 ppm. This amount corresponded to approximately six percent of the total sludge weight on a dry basis. The air flow rate was reduced from 2,500 to about 280 cc/min, and the stirring rate was held constant at 300 rpm. Under these conditions, the degree of agitation necessary to keep the seed material in suspension was minimized. Sufficient hydrated lime was added to the stirred, aerated suspension to achieve a final pH of 7.8. It was found necessary to increase the reaction time from 30 to 60 minutes to achieve complete oxidation and precipitation of iron; this may have been due to the lower aeration rate and the fact that, at the lower speed, the stirrer was less effective in breaking up small agglomerated particles of lime in the suspension. After the 60-minute reaction period, the entire sample was transferred to a 1,000-ml graduated cylinder and the sludge was allowed to settle for 30 minutes. Measurements were made of settling rate, settled sludge volume, sludge solids content, and supernatant liquid turbidity after the 30-minute settling period.

In tests on the effect of seed crystal quantity, the 200 x 325 mesh sieve fraction was used throughout and the amount of seeding material employed was increased through the range of 100 to 2,000 ppm. All other steps in the experimental procedure remained as described above.

In tests on the effect of stirring rate, the stirring rate was increased through the range 300 to 480 rpm. The aeration rate was kept at about 280 cc/min and the 200 x 325 mesh sieve fraction of the seed material was used in all tests at a concentration of 2,000 ppm. All other conditions remained as described earlier. For purposes of comparison, a few tests were conducted to observe the effect of stirring rate alone on unseeded (control) samples.

Finally, a few experiments were conducted using as seeding materials two actual sludge samples which had been obtained from lime neutralization of the synthetic mine water. One of the samples had been recovered after a freeze-dewatering experiment. Both sludge samples were filtered, air-dried, and ground to a powder. After they had been sieved, the samples were found to consist predominantly of minus 325 mesh material, thus the 325 mesh x 0 particle size fraction was used for these tests. The aeration and stirring rates employed were 280 cc/min and 300 rpm, respectively.

Sludge Heating and Freezing

In the sludge heating studies, tests were grouped into three series according to experimental procedure. The first series involved heating the synthetic mine water samples before lime addition and iron precipitation. Hydrated lime, in an amount sufficient to produce a final pH of 7.8, was added with stirring and aeration to 1,000-ml batch samples of the mine water which had been previously heated to the desired temperature. Temperature was maintained constant during a 30-minute reaction period, after which the sample was gradually cooled to room temperature over a one-hour period with the aid of a cold tap water bath. The sludge suspension was then transferred to a 1,000-ml graduated cylinder, and measurements were made of sludge settling rate, 30-minute settled sludge volume, sludge solids content, and supernatant liquid turbidity after the 30-minute settling period. A portion of the sludge was filtered using a Millipore filter assembly, and the filter cake was air-dried at room temperature, pulverized to a powder, and subjected to x-ray diffraction analysis.

The second series of experiments involved preparation of the sludges at room temperature and heating the sludge concentrates. Sludges were prepared by adding hydrated lime to 1,000-ml samples of the snythetic coal mine water, followed by a 30-minute aeration period with stirring. The sludge was allowed to settle for 30 minutes, then the supernatant liquid was siphoned off and the remaining sludge concentrate (about 200 ml) was transferred to a 250-ml beaker and heated to the desired temperature with stirring. The sludge was kept at the elevated temperature for 10 minutes, and was then cooled to room temperature again. Finally, the sample was stirred, a 100-ml portion was transferred to a 100-ml graduated cylinder, and settling rate, 30-minute settled sludge volume, and sludge solids content were measured. In addition, samples of the settled sludge were prepared for x-ray diffraction analysis as described above. It was not possible to conduct turbidity determinations in this series of tests, since the volume of supernatant liquid remaining in the 100-ml graduated cylinder after 30 minutes was not sufficient to provide the required amount of sample (about 30 ml) for the turbidimeter.

The third series of experiments involved essentially a variation on those conducted during the second series. Sludge samples were prepared, concentrated, and heated in the same manner as described in the preceding paragraph. However, instead of being first cooled to room temperature, the sludges (100-ml portions) were transferred immediately to the 100-ml graduated cylinder while still warm and settling behavior was observed for the usual 30-minute period. After the sample for solids content measurement had been taken, the sludge was left undisturbed for an additional 30-minute period to allow further cooling to room temperature. The sample was then made up to volume (100 ml) using portions of the supernatant liquid which had been saved from the original sludge concentration step; the sludge was resuspended, and settling rate, sludge volume, and solids content were measured again.

In the sludge freezing experiments, sludges were prepared in the usual manner by hydrated lime treatment of synthetic and actual mine waters. Sludges were allowed to settle for some specified time period, then the settled sludge was recovered by decantation and frozen at -4.4 C (24 F) in a refrigerator freezer compartment. Once frozen, the samples were removed from the freezer and allowed to thaw gradually without agitation at room temperature. No attempt was made to control the rates of sludge freezing or thawing.

Miscellaneous Approaches - Coprecipitation of Calcium Carbonate

In the experiments on the effect of calcium carbonate coprecipitation during lime neutralization, 1,000-ml batch samples of both synthetic and actual (Keystone) mine waters, were used. Into one sample, carbon dioxide gas (Matheson "Coleman Instrument Grade," 99.99 percent minimum purity) was bubbled at room temperature for a predetermined time period (CO_2 flow rate = 2.0 scfh or 944 cc/min). After the CO_2 purge period, hydrated lime was added and the sample was aerated with stirring for 30 minutes. The lime was added as a dry powder in the earlier experiments, but it tended to agglomerate and pH control was difficult. Consequently, in later experiments the lime was sieved to minus 325 mesh and added to the mine water sample as a slurry in deionized water. After the 30-minute reaction period, the sample was transferred to a 1,000-ml graduated cylinder for measurement of settling rate, settled sludge volume, sludge solids content, and supernatant liquid turbidity after the 30-minute settling period. In most cases, control samples without prior CO_2 treatment were tested simultaneously for comparison.

SECTION V

RESULTS AND DISCUSSION

Magnetic Sludge Studies

Magnetic Sludge Factorial Experiment

The initial results from the magnetic sludge factorial experiment are summarized in Table 2. For ease in interpretation, the four separate variables are identified with the high and low level of each variable being represented by + and - signs, respectively. Several important relationships are evident from an inspection of the data in Table 2. For example, magnetic sludges were obtained only during the high temperature tests. Secondly, with the exception of the last three tests, there is an apparent correlation between settled sludge volume (or sludge settling rate) and pH.

Data on residual dissolved Fe^{2+} indicate that precipitation of iron is not complete at pH 8 and room temperature (Tests 1, 3, 5, and 7). Although this should not have any confounding effect on the interpretation of the results, it is an important observation and an aspect of the overall conceptual process that should be considered carefully during any future developmental work.

The data in Table 2 were employed more fully in the calculation of main effects and variable interactions for each of the three responses. For this purpose, a codified design and calculation matrix, shown in Table 3, was used. The derivation of this matrix is described by Davies.(9) The positive or negative signs for variable interactions are obtained simply by algebraic multiplication of the signs for each single variable involved in the interaction. Main effects and interactions are calculated by multiplying the response values (Table 2) by the corresponding effect elements (Table 3), summing the results, and dividing by 8. The resulting value for single variables is also sometimes designated as an average effect, since (for two levels of the variable only) it is simply the difference between the average response of all trials carried out at the first level of the variable (factor) and that of all trials at the second level. If the effect of one variable changes at different levels of another variable, the two variables are said to interact. The relative importance of the variable or variables in question is reflected by the absolute magnitude of the calculated main effect or interaction. First-order (two variable) interactions are usually easy to interpret in terms of the physical behavior of the system. Second- and higher-order interactions are often less readily understood, and are often of minor significance in any case.

The main effects and interactions derived from the present study in the manner described above are listed in Table 4. It should be noted that

TABLE 2. RESULTS OF FACTORIAL EXPERIMENT ON VARIABLES AFFECTING MAGNETIC SLUDGE FORMATION

Test	Variables*				Responses			Residual Dissolved Fe^{2+} ppm
	1	2	3	4	60-Min Settled Sludge Volume Percent**	Sludge Settling Rate, cm/min	Magnetic Response	
1	-	-	-	-	15.0	0.08	0.00	16
2	+	-	-	-	19.0	0.02	0.00	< 1
3	-	+	-	-	18.2	0.03	0.00	6
4	+	+	-	-	18.7	0.02	0.00	< 1
5	-	-	+	-	13.0	0.11	0.00	14
6	+	-	+	-	18.8	0.02	0.00	< 1
7	-	+	+	-	18.3	0.03	0.00	3
8	+	+	+	-	19.0	0.02	0.00	< 1
9	-	-	-	+	5.1	2.43	4.06	< 1
10	+	-	-	+	13.6	0.16	0.29	< 1
11	-	+	-	+	11.6	0.15	2.46	< 1
12	+	+	-	+	18.8	0.02	< 0.01 †	< 1
13	-	-	+	+	17.2	0.05	2.10	< 1
14	+	-	+	+	11.8	0.19	0.09	< 1
15	-	+	+	+	18.4	0.02	0.61	< 1
16	+	+	+	+	12.1	0.34	0.00	< 1

* Variable Identification

Variable	Levels	
	+	-
1 = pH	10.0	8.0
2 = Al/Fe Ratio	0.15	0.05
3 = Mg/Fe Ratio	1.5	0.5
4 = Temperature	90 C	25 C

** Based on a total suspension volume of 500 ml

† Very weak magnetic response, below the sensitivity of the balance, was detected by visual observation.

TABLE 3. CODIFIED DESIGN AND CALCULATION MATRIX

	Variables				Interactions										
Test	1	2	3	4	(1,2)	(1,3)	(1,4)	(2,3)	(2,4)	(3,4)	(1,2,3)	(2,3,4)	(1,2,4)	(1,3,4)	(1,2,3,4)
1	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+
2	+	-	-	-	-	-	-	+	+	+	+	-	+	+	-
3	-	+	-	-	-	+	+	-	-	+	+	+	+	-	-
4	+	+	-	-	+	-	-	-	-	+	-	+	-	+	+
5	-	-	+	-	+	-	+	-	+	-	+	+	-	+	-
6	+	-	+	-	-	+	-	-	+	-	-	+	+	-	+
7	-	+	+	-	-	-	+	+	-	-	-	-	+	+	+
8	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-
9	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-
10	+	-	-	+	-	-	+	+	-	-	+	+	-	-	+
11	-	+	-	+	-	+	-	-	+	-	+	-	-	+	+
12	+	+	-	+	+	-	+	-	+	-	-	-	+	-	-
13	-	-	+	+	+	-	-	-	-	+	+	-	+	-	+
14	+	-	+	+	-	+	+	-	-	+	-	-	-	+	-
15	-	+	+	+	-	-	-	+	+	+	-	+	-	-	-
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Designation of Variables:
1 = pH
2 = Al/Fe Ratio
3 = Mg/Fe Ratio
4 = Temperature

TABLE 4. MAIN EFFECTS AND INTERACTIONS BASED ON DATA FROM MAGNETIC SLUDGE FACTORIAL EXPERIMENT

	Responses					
	Settled Sludge Volume Percent		Sludge Settling Rate		Magnetic Response	
	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions
Single Variable:	4	-4.22	4	0.38	4	1.08
	2	3.00	2	-0.31	1	-0.99
	1	2.17	1	-0.27	3	-0.62
	3	0.77	3	-0.26	2	-0.32
Two Variable Interactions:	1,3	-2.87	1,3	0.35	1,4	-0.99
	1,2	-1.65	1,2	0.31	3,4	-0.62
	3,4	1.22	2,3	0.31	1,3	0.57
	2,4	0.90	2,4	-0.27	2,4	-0.32
	2,3	-0.65	3,4	-0.27	1,2	0.22
	1,4	-0.57	1,4	-0.22	2,3	0.16
Three Variable Interactions:	1,3,4	-3.37	1,3,4	0.36	1,3,4	0.57
	2,3,4	-1.30	2,3,4	0.32	1,2,4	0.22
	1,2,4	0.50	1,2,4	0.28	2,3,4	0.16
	1,2,3	-0.45	1,2,3	-0.24	1,2,3	-0.11
Four Variable Interaction:	1,2,3,4	-0.05	1,2,3,4	-0.24	1,2,3,4	-0.11

Designation of Variables: 1 = pH
2 = Al/Fe Ratio
3 = Mg/Fe Ratio
4 = Temperature

these initial results were refined by data from later replications (to be discussed below). As indicated by Table 4, the main effects and interactions for each response are grouped according to the number of variables involved and are listed in order of decreasing absolute magnitude in each group. The results will be discussed below in terms of each response.

Settled Sludge Volume

The data in Tables 2 and 4 indicate that the most significant variable affecting settled sludge volume is temperature. The negative value for the temperature main effect simply means that settled sludge volume was significantly greater at the lower level of temperature (25 C in this experiment). This effect is particularly apparent if one compares Test 6 with Test 14 (settled sludge volumes of 18.8 and 11.8 percent, respectively) and Test 8 with Test 16 (settled sludge volumes of 19.0 and 12.1 percent, respectively). The sludges from each of these four tests were all essentially nonmagnetic. It is believed that these differences are due to coprecipitation of gypsum during the higher temperature tests, and this will be discussed further below.

Other single variables significantly affecting settled sludge volume are Al/Fe ratio and pH, in order of decreasing importance. Both main effects are positive, indicating an increasing sludge volume with both increasing pH and aluminum concentration. Ostensibly, there is no reason why an increase in pH should result in greater sludge volumes, if all other conditions are held constant. The explanation lies in the appearance of a significantly large first-order interaction between pH and the Mg/Fe ratio. This interaction was expected, and is consistent with the fact that $Mg(OH)_2$ precipitates at about pH 9.6. This same situation is reflected by the relatively large second-order interaction involving pH, Mg/Fe ratio, and temperature.

Sludge Settling Rate

A relationship between sludge settling rate and settled sludge volume would be expected, and this is evidenced by the close correspondence in the ranking of main effects and interactions within a given group. Thus, statements made previously regarding sludge volume would hold generally in this case, with the understanding that effects or interactions contributing to high sludge volumes also lead to low settling rates (indicated by the reversal of signs).

Magnetic Response

Again, the data indicate that temperature is the most important variable affecting magnetic response. This would seem obvious from the fact that no magnetic sludges were obtained in the lower temperature tests (Table 2). In this case, however, pH appears to be the second most important variable, and the main effect of -0.99 indicates that increasing pH to the higher level produced a marked decrease in the magnetic properties of the product. The effect of increasing magnesium concentration is third in importance, and is also reflected in the relatively large 1,3 and 1,3,4 variable interactions. It was anticipated that these interactions would be significant, in view of the reported ability of magnesium to inhibit the formation of magnetite from aqueous suspension when the pH is high enough (> 9.6) to allow precipitation of $Mg(OH)_2$.(2,4)

Other major interactions affecting magnetic response are the pH, temperature [1,4] and the Mg/Fe ratio, temperature [3,4] interactions. The 1,4 interaction (negative) may be interpreted as follows: the effect of higher temperature in increasing the magnetic response of the product is greater at the lower pH level, or conversely, the effect of higher pH in decreasing the magnetic response is greater at the lower temperature level. The 3,4 interaction may be interpreted in a similar manner if one substitutes "Mg/Fe ratio" for "pH" in the preceding sentence. The positive value for the 1,3 interaction indicates that both variables are operating in the same direction, that is, magnetic response is affected adversely when both variables are at their higher levels. This is presumably related to the precipitation of $Mg(OH)_2$ at the higher pH level, as was indicated previously. All other variable interactions, and those involving the Al/Fe ratio in particular, appear to be less important in terms of their effect on magnetic response.

All tests at the higher temperature level (Tests 9 through 16, Table 2) were replicated. The results of these replications are shown in Table 5 under the headings "Trial 2." Also shown in Table 5 are the mean values obtained for each response. These mean values were used in a complete recalculation of the main effects and interactions of the four independent variables considered in this study (pH, Al/Fe and Mg/Fe molar ratios, and temperature). The results of these calculations are shown in Table 6.

A comparison of the results in Table 6 with those derived earlier (Table 4) reveals that, in nearly every case, the rankings and signs of main effects and interactions within a given group remain virtually unchanged from those determined before the data were refined. The only exceptions to this statement involve a few first-order (two-variable) and higher-order interactions which were judged to be not significant in the original interpretation of the results.

The important trends noted as a result of these revised calculations are as follows:

In general, the absolute magnitudes of all main effects and interactions decreased slightly. In other words, there was a tendency for small effects and interactions to more closely approach a value of zero (nonsignificance).

TABLE 5. COMPARISON OF RESULTS OBTAINED BY PARTIAL REPLICATION OF MAGNETIC SLUDGE FACTORIAL EXPERIMENT

Test	Variables*			Responses								
				Settled Sludge Volume Percent**			Sludge Settling Rate, cm/min			Magnetic Response		
	1	2	3	Trial 1	Trial 2	Mean	Trial 1	Trial 2	Mean	Trial 1	Trial 2	Mean
9	-	-	-	5.1	6.5	5.80	2.43	1.02	1.725	4.06	3.87	3.965
10	+	-	-	13.6	17.3	15.45	0.16	0.04	0.100	0.29	0.25	0.270
11	-	+	-	11.6	11.2	11.40	0.15	0.16	0.155	2.46	2.61	2.535
12	+	+	-	18.8	18.7	18.75	0.02	0 02	0.020	< 0.01	< 0.01	< 0.010†
13	-	-	+	17.2	17.4	17.30	0.05	0.04	0.045	2.10	1.77	1.935
14	+	-	+	11.8	12.6	12.20	0.19	0.19	0.190	0.09	0.00	0.045
15	-	+	+	18.4	18.0	18.20	0.02	0.03	0.025	0.61	0.79	0.700
16	+	+	+	12.1	12.8	12.45	0.34	0.28	0.310	0.00	0.00	0.000

* Variable Identification

Variable	Levels	
	+	-
pH	10.0	8.0
Al/Fe Ratio	0.15	0.05
Mg/Fe Ratio	1.5	0.5

(Temperature = 90 C for all tests)

** Based on a total suspension volume of 500 ml.

† Very weak magnetic response, below the sensitivity of the balance, was detected by visual observation.

TABLE 6. REVISED CALCULATION OF MAIN EFFECTS AND INTERACTIONS BASED ON DATA FROM MAGNETIC SLUDGE FACTORIAL EXPERIMENT

	Responses					
	Settled Sludge Volume Percent		Sludge Settling Rate		Magnetic Response	
	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions
Single Variable:	4	-3.55	4	0.28	4	1.18
	2	2.30	2	-0.21	1	-1.10
	1	2.15	1	-0.19	3	-0.51
	3	0.87	3	-0.17	2	-0.37
Two Variable Interactions:	1,3	-3.22	1,3	0.27	1,4	-1.10
	1,2	-1.45	1,2	0.22	3,4	-0.51
	3,4	1.32	2,3	0.22	1,3	0.45
	2,3	-0.62	3,4	-0.18	2,4	-0.37
	1,4	-0.60	2,4	-0.18	1,2	0.29
	2,4	0.12	1,4	-0.15	2,3	0.05
Three Variable Interactions:	1,3,4	-3.72	1,3,4	0.28	1,3,4	0.45
	2,3,4	-1.27	2,3,4	0.22	1,2,4	0.29
	1,2,4	0.70	1,2,4	0.19	2,3,4	0.05
	1,2,3	0.02	1,2,3	-0.17	1,2,3	0.00
Four Variable Interaction:	1,2,3,4	0.42	1,2,3,4	-0.17	1,2,3,4	0.00

Designation of Variables: 1 = pH
2 = Al/Fe Ratio
3 = Mg/Fe Ratio
4 = Temperature

With regard to the settled sludge volume, the main effect of the Mg/Fe ratio (variable 3) increased slightly. This was also reflected by increases in the absolute values of certain interactions involving this variable, notably the 1,3 (pH, Mg/Fe) interaction. Thus, these interactions which were found to be important in the original analysis involving single trials only, now assume an even greater importance based on the revised calculations.

With regard to magnetic response, revised calculations show slight increases in the absolute values of the main effects for variables 1, 2, and 4. Correspondingly, all interactions involving combinations of these variables were also found to be slightly larger. These findings do not alter the conclusions drawn from the original analysis of the data from single trials. However, the revised calculations do indicate that the effect of aluminum on magnetic response is slightly more important (relative to the effect of magnesium) than was suggested by the original analysis.

The data obtained from the partial replication of the factorial experiment may be employed to compute error terms for each of the three responses. To accomplish this, and since only the high temperature tests were replicated, it is appropriate to consider the last eight tests (Tests 9 through 16) as a separate factorial experiment involving three variables (temperature held constant) at two levels each, i.e., as a 2^3 factorial experiment. Main effects and interactions of the three variables are then computed in the usual manner for each response.

The results of such computations are shown in Table 7, together with the error terms for the 95 percent confidence interval (95 percent C.I.). These error terms are derived by calculating the variance for each test, pooling these variances, and determining the variance of main effects or interactions, according to the procedure outlined by Pavelic and Saxena.(6) Main effects and interactions which are larger than the error term, indicated by the asterisks in Table 7, are assumed to be significant at the 95 percent confidence level.

Several interesting comparisons can be made between the results of the full (2^4) factorial in Table 6 and those of the partial (2^3) factorial in Table 7. For example, the importance of the 1,3 interaction is evident in all cases. For magnetic response, the ranking of single variables in both cases is identical. However, for the other two responses, variable 3 apparently assumes greater significance when temperature is held constant at the higher level. This fact, in conjunction with the significant 2,3 interaction for sludge volume, suggests that the physical behavior of the sludge may be more sensitive to changes in both Mg and Al concentrations at the higher temperature than at the lower temperature. One possible explanation for this involves the tendency toward coprecipitation of gypsum at the higher temperature level and its effect on sludge properties (discussed below).

TABLE 7. MAIN EFFECTS AND INTERACTIONS FOR THE 2^3 FACTORIAL EXPERIMENT INVOLVING HIGH TEMPERATURE TESTS ONLY

	Responses					
	Settled Sludge Volume Percent		Sludge Settling Rate		Magnetic Response	
	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions
Single Variable:	2	2.50*	2	-0.39	1	-2.20*
	3	2.20*	3	-0.35	3	-1.02*
	1	1.55*	1	-0.33	2	-0.75*
Two Variable Interactions:	1,3	-6.95*	1,3	0.54*	1,3	0.91*
	2,3	-1.90*	2,3	0.44	1,2	0.59*
	1,2	-0.75	1,2	0.41	2,3	0.11
Three Variable Interaction:	1,2,3	0.45	1,2,3	-0.34	1,2,3	0.00
Error Term (95% C.I.)		±1.19		±0.53		±0.13

* Probably significant effects or interactions based on error term.

Designation of Variables:
1 = pH
2 = Al/Fe Ratio
3 = Mg/Fe Ratio

Overall Significance of the Results

The magnetic sludge factorial experiment and replications yielded valuable data concerning certain variables which affect the formation and settling behavior of the magnetic product. In addition, certain design parameters for a conceptual treatment process for coal mine drainage may be inferred from the results.

For example, it is significant that temperature was found to be the most important variable affecting all three responses, indicating that a conceptual magnetic sludge process should include a sludge heating step. The effect of pH is also relatively important, particularly as related to magnetic response of the product. The pH effect is in turn reflected in the 1,3 interaction, which was found to be significant for all thr e responses. These findings indicate that the pH should be high enough to afford complete precipitation of iron (as Fe^{2+}) but low enough to avoid coprecipitation of $Mg(OH)_2$. Experience has shown that the optimum pH is about 8.5.

It should be noted that another phenomenon was observed during these experiments which complicated interpretation of the results. This involved the occasional presence of coprecipitated gypsum ($CaSO_4 \cdot 2H_2O$) in the sludge and its effect on the measured settling rates. In each of the high temperature, high pH tests (including replications) a whitish, granular material was observed during settling rate measurements. This material was usually dispersed throughout the bulk of the sludge volume, but in at least one case (Test 16) it settled rapidly to deposit as a discrete layer at the bottom of the graduated cylinder. A portion of this material was separated by centrifugation and identified as gypsum by x-ray diffraction analysis. The tendency of this coprecipitate to settle at a faster rate than the bulk of the sludge probably accounts for the deviations from the established trends for sludge volumes and settling rates encountered in the later tests, especially Tests 14 and 16 (Table 2). This belief is reinforced by another observation: in at least two tests (Tests 10 and 14) the sludge settled rather slowly for about 40 minutes, but as settling rate measurements were commenced (after the sludge-liquid boundary passed the 100 ml mark of the graduated cylinder) the rate increased considerably. This behavior may have been the result of gradual crystallization of gypsum from a supersaturated solution, a tendency which is characteristic for this compound. Coprecipitated gypsum was not observed in any of the lower-temperature tests, consistent with the fact that its solubility increases with decreasing temperature.

Ideally, aluminum and magnesium should be absent from the system, although the data show that it is possible to obtain a sludge exhibiting some magnetic response when small amounts of aluminum and magnesium are present. Consequently, the next logical step in the program was to ascertain the limits to which these impurities could be tolerated based on their effects on magnetic response and other properties of the sludge obtained under the conditions cited above.

Effects of Magnesium and Aluminum Interference

Tolerance Level for Magnesium

A series of tests was conducted at pH 8 and 90 C to study the effect of increasing the Mg/Fe molar ratio on magnetic sludge properties. The experiments were run using synthetic mine water solutions containing only dissolved ferrous and magnesium sulfates (i.e., aluminum was absent from the system). The results of these tests are shown in Table 8 and Figure 3. The data reveal that the effect of magnesium on magnetic response and other sludge properties is certainly not negligible at pH 8. This result was somewhat unexpected in view of reports that the interference is restricted to pH values at which magnesium is precipitated as the hydroxide (pH > 9.6).(2,4).

As reflected in Table 8, there was a gradual lightening in color and a rapid increase in settled volume of the precipitate as the Mg/Fe molar ratio increased. A marked discontinuity in the settled sludge volume curve, indicated by the dashed line in Figure 3, is believed to be due to the effect of coprecipitated gypsum at the higher magnesium concentrations. Small, granular gypsum particles were observed dispersed throughout the sludge in the tests at Mg/Fe molar ratios of 5 and 10. The effect of this coprecipitate in increasing settling rates and decreasing sludge volumes has been mentioned previously; Figure 3 shows striking graphic evidence of the nature of this effect.

Based on the results of these experiments on the effect of magnesium on magnetic sludge formation, it would appear that there is no well-defined tolerance limit for this impurity. Figure 3 shows that the decrease in magnetic response is gradual as the Mg/Fe molar ratio increases. In fact, when magnetic response was observed qualitatively with a small hand magnet, the behavior of all samples prepared at a Mg/Fe molar ratio of 2.5 and below appeared to be essentially identical.

The results shown by Figure 3 suggest that a practical (although perhaps conservative) tolerance level for magnesium would be that corresponding to a Mg/Fe molar ratio of 1.0. This value is in accord with that reported by Kakabadse et al.,(4) although it should be recognized that these investigators employed substantially different experimental conditions than those of the present study. Our data (Figure 3) show that magnetic response at the molar ratio Mg/Fe = 1.0 is roughly only 40 percent of that measured when magnesium was completely absent from the system.

On the basis of the present studies, the interference due to magnesium would appear to involve the cation Mg^{2+} via a solution mechanism. This actually would seem to be more consistent with the proposed mode of magnesium interference, which involves substitution by Mg^{2+} for Fe^{2+} in the magnetite lattice,(4) than would a mechanism involving solid magnesium hydroxide. At any rate, magnesium interference is presumably of

TABLE 8. EFFECT OF THE Mg/Fe MOLAR RATIO ON MAGNETIC SLUDGE PROPERTIES

Test No.	Mg/Fe Molar Ratio	mg/l Mg per 100 mg/l Fe	60-Minute Settled Sludge Volume Percent‡	Sludge Settling Rate, cm/min	Magnetic Response*	Color of Dried Sludge
Control	0.00	0.0	0.8	†	8.58	black
397-60	0.50	21.8	5.0	4.1	4.90	dark brown
397-59	1.50	65.3	12.6	0.12	2.76	medium brown
397-58	2.50	108.8	16.7	0.05	1.65	medium brown
397-56	5.00	217.6	8.2**	0.64	0.34	light brown
397-53	10.00	435.2	12.5**	0.16	0.12	beige

‡ Based on a total suspension volume of 500 ml.

* Measured on a 0 200 gram sample.

† Indistinct sludge-liquid boundary prevented settling rate measurement.

** Granular gypsum was observed dispersed throughout the sludge.

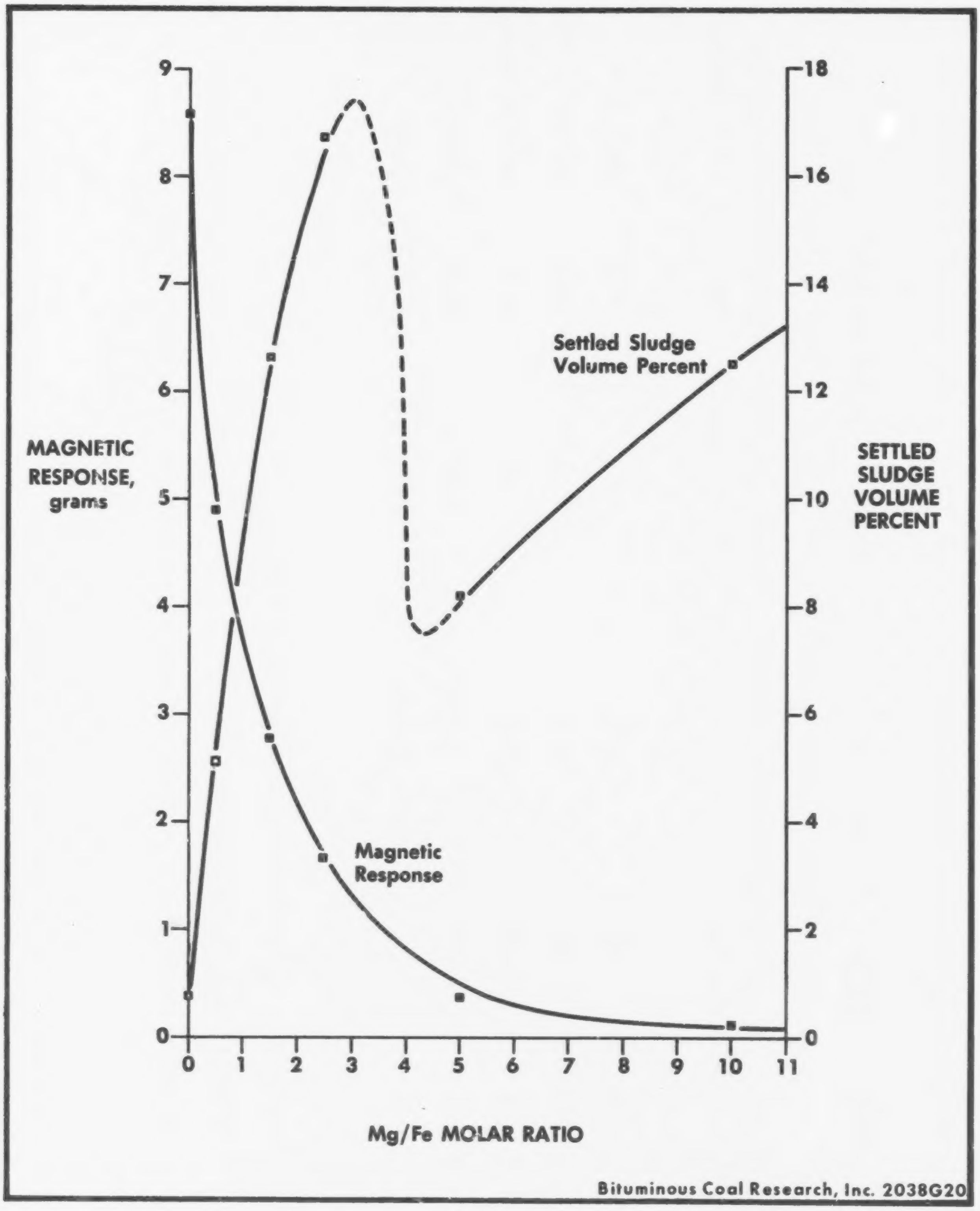

Figure 3. Magnetic Response and Settled Sludge Volume Percent as Functions of the Mg/Fe Molar Ratio

much greater consequence at higher pH values. This is indicated by the observations of Kakabadse et al. (2,4) as well as by the results of our own factorial experiment.

Results of chemical analyses of sludges obtained in this series of tests are presented in Table 9. Interestingly, although all of the magnesium was presumably in solution under the experimental conditions employed, the data indicate that approximately one-half of the magnesium available during magnetic sludge formation is present in the sludge. The magnesium content of the sludges increased regularly with increasing Mg/Fe ratios, although the presence of coprecipitated gypsum in the last two sludges in the series led to anomalously low values for both iron and magnesium contents.

Tolerance Level for Aluminum

Another series of tests was conducted at pH 8 and 90 C to study the effect of increasing the Al/Fe molar ratio on sludge properties. Synthetic mine water solutions containing only ferrous and aluminum sulfates (no magnesium) were used in these experiments. The results are shown in Table 10 and Figure 4.

As indicated by Figure 4, magnetic response decreases and settled sludge volume increases as the Al/Fe molar ratio increases. These results are very similar to those from the tests on increasing Mg/Fe molar ratios, presented in the preceding section. However, there is an important difference in the magnitudes of the two effects. This is illustrated in Figure 5, which shows the Al/Fe and Mg/Fe molar ratios plotted on the same scale. It is obvious from Figure 5 that, on a mole-to-mole basis and under the experimental conditions employed, the effect of aluminum on magnetic properties of the sludge is much more pronounced than that due to magnesium. Interestingly, 60-minute settled sludge volumes were roughly the same at a given value of the Al/Fe or Mg/Fe molar ratio; in no case was coprecipitated gypsum observed during this series of tests on increasing Al/Fe ratios.

Again, there is no clear-cut tolerance limit for aluminum. However, in line with the example given earlier for magnesium interference, the point at which magnetic response is 40 percent of that of the control sample (from Figure 4) corresponds to an Al/Fe molar ratio of about 0.18. It is noteworthy that Stauffer and Lovell (5) have reported, based on qualitative observations, that the ferromagnetic properties of products prepared in a similar manner diminished rapidly as the Al/Fe molar ratio increased, and were "so slight as to be inconsequential" at an Al/Fe molar ratio of 0.184.

Results of chemical analyses of sludges obtained in this series of tests are presented in Table 11. The data show that, as expected, essentially all of the aluminum present in the original solution reports to the sludge, presumably as coprecipitated $Al(OH)_3$.

TABLE 9 EFFECT OF INCREASING Mg/Fe MOLAR RATIO ON CHEMICAL COMPOSITION OF THE MAGNETIC SLUDGE

Test No.	Mg/Fe Molar Ratio During Sludge Preparation	Mg/Fe Molar Ratio in Sludge	Weight Percent of Indicated Constituent in Sludge		
			Fe	Mg	Ca
397-60	0.50	0.25	53.2	5.8	3.5
397-59	1.50	0.67	39.7	11.6	2.4
397-58	2.50	1.13	32.4	16.0	2.7
397-56	5.00	1.95	13.1	11.1	11.1*
397-53	10.00	4.96	5.0	10.8	16.3*

* Coprecipitated gypsum was detected visually in these two samples

TABLE 10. EFFECT OF THE Al/Fe MOLAR RATIO ON MAGNETIC SLUDGE PROPERTIES

Test No.	Al/Fe Molar Ratio	mg/l Al per 100 mg/l Fe	60-Minute Settled Sludge, Volume Percent*	Sludge Settling Rate, cm/min	Magnetic Response**	Color of Dried Sludge
Control	0.00	0.0	0.8	†	8.58	black
397-61	0.05	2.4	1.0	†	8.24	black
397-64	0.10	4.8	1.2	†	6.36	black
397-62	0.15	7.2	1.5	†	4.84	brownish-black
397-63	0.30	14.4	2.9	1.95	0.65	reddish-brown
397-65	0.50	24.0	6.6	0.88	0.10	yellowish-brown

* Based on a total suspension volume of 500 ml.

** Measured on a 0.200 gram sample.

† Indistinct sludge-liquid boundary prevented settling rate measurement

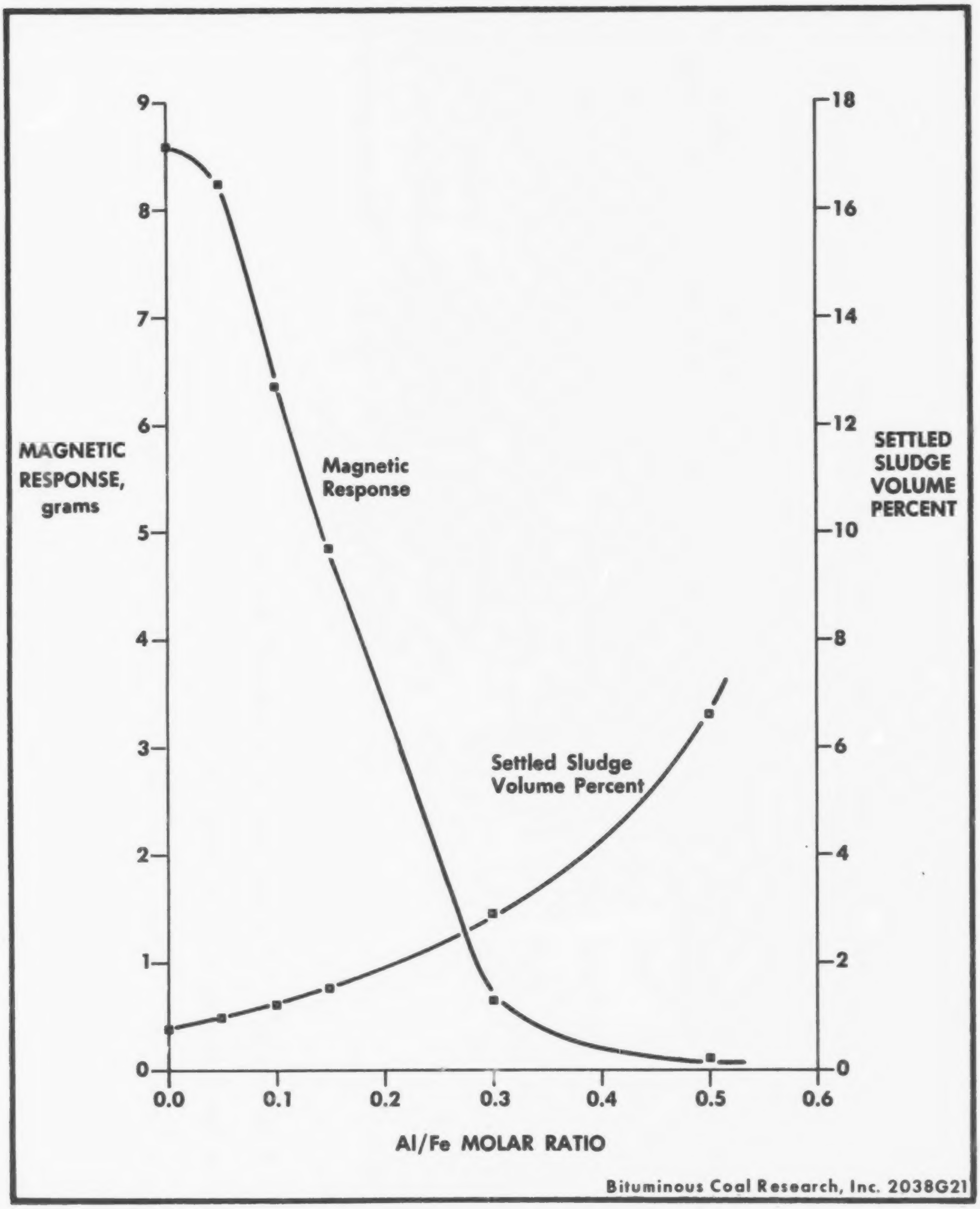

Figure 4. Magnetic Response and Settled Sludge Volume Percent as Functions of the Al/Fe Molar Ratio

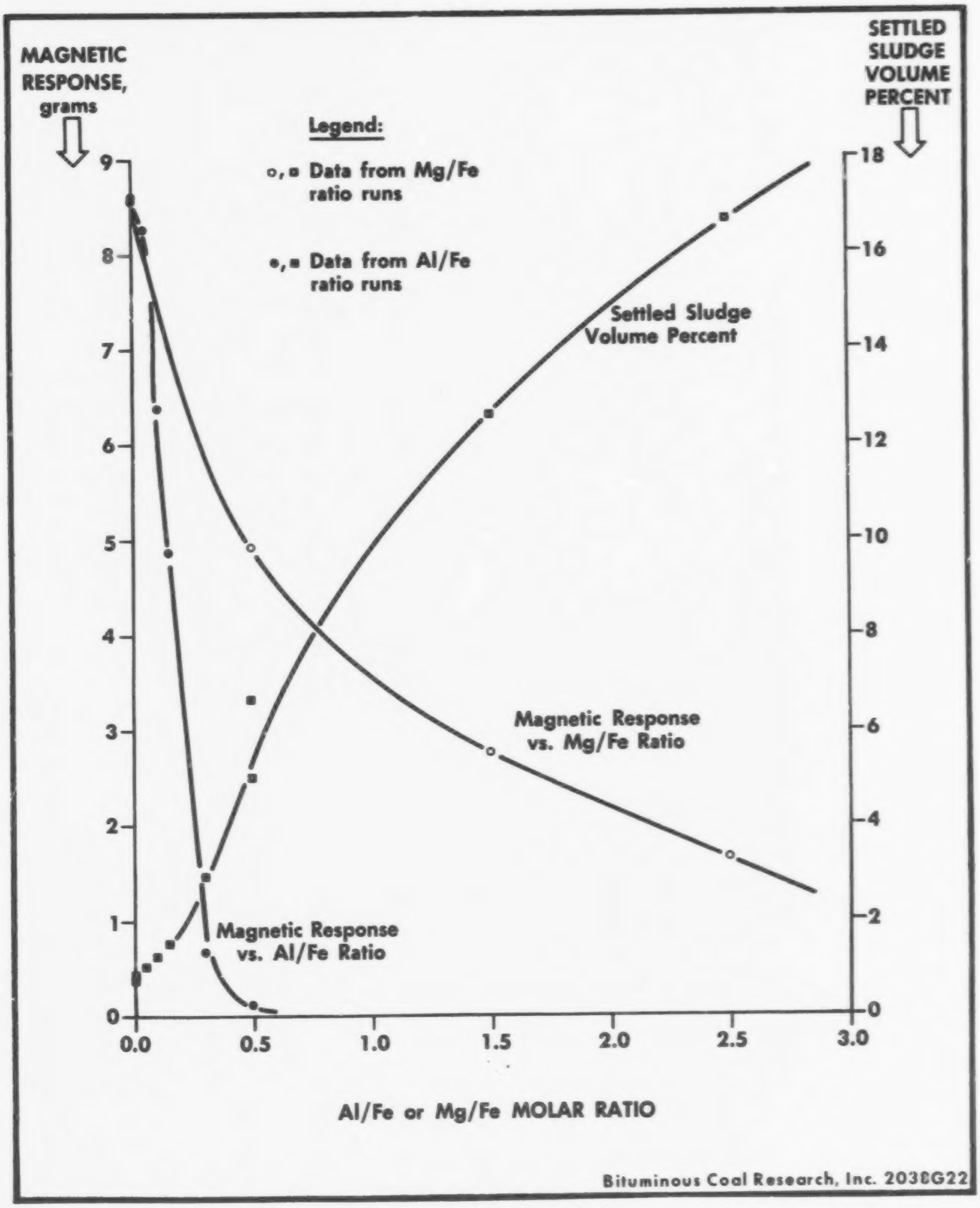

Figure 5. Magnetic Response and Settled Sludge Volume Percent as Functions of the Al/Fe and Mg/Fe Molar Ratios

TABLE 11. EFFECT OF INCREASING Al/Fe MOLAR RATIO ON CHEMICAL COMPOSITION OF THE MAGNETIC SLUDGE

Test No.	Al/Fe Molar Ratio During Sludge Preparation	Al/Fe Molar Ratio in Sludge	Weight Percent of Indicated Constituent in Sludge		
			Fe	Al	Ca
397-61	0.05	0.05	57.4	1.4	2.9
397-64	0.10	0.09	61.1	2.6	4.0
397-62	0.15	0.13	55.2	3.5	4.2
397-63	0.30	0.30	45.7	6.6	3.4
397-65	0.50	0.46	35.1	7.8	5.2

Correlation Between Magnesium and Aluminum Interferences

For the purpose of predicting whether a given mine water might be amenable to treatment by a magnetic sludge process, some correlation between magnesium interference and aluminum interference would be desirable. The data suggest that the effects are additive, but that the effect of aluminum must be weighted more heavily than the effect of magnesium.

Through a consideration of the results shown by Figure 5, it was found that the following relationship existed for a given value of the magnetic response:

$$\mathrm{Mg/Fe} = k(\mathrm{Al/Fe})^2$$

where k was approximately constant with a value of 30 ± 5. Consequently, data from the tests on the effect of aluminum were revised according to the above relationship and plotted as a function of the magnetic response of the samples, as shown by Figure 6. In a similar fashion, data from the tests at pH 8 and 90 C obtained during the earlier factorial experiment (Tests 9, 11, 13, and 15, Table 5) were included in the calculations and are also shown in Figure 6. These data are significant in that both aluminum and magnesium were present at varying concentrations during the magnetic sludge preparations, thereby affording a test of the hypothesis that the interference effects are additive. In spite of some scattering of the points around the smooth curve, it is apparent that a reasonably good correlation is possible. Of particular significance is the fact that the data points from the factorial experiment also tend to follow the curved line.

The results shown by Figure 6 suggest that, as a first approximation, the tolerance levels for aluminum and/or magnesium can be defined empirically in terms of their molar ratios with iron by means of the following expression:

$$\mathrm{Mg/Fe} + 30(\mathrm{Al/Fe})^2 \leq 1.0$$

In the absence of aluminum, the tolerance level for magnesium would be that concentration corresponding to a Mg/Fe molar ratio of 1.0. This value was suggested earlier as a practical limitation for magnesium interference. In the absence of magnesium, the corresponding value for the Al/Fe molar ratio would be the square root of 0.0333 or 0.182, which was also derived earlier from a consideration of the data on aluminum interference alone.

It should be emphasized that the relationships shown above are only valid for the experimental conditions employed, i.e., where the entire mine water sample was heated before lime alkalization. Under these conditions, magnesium was always present in the system, presumably as Mg^{2+} at pH 8. In later studies, to be discussed below, it was found

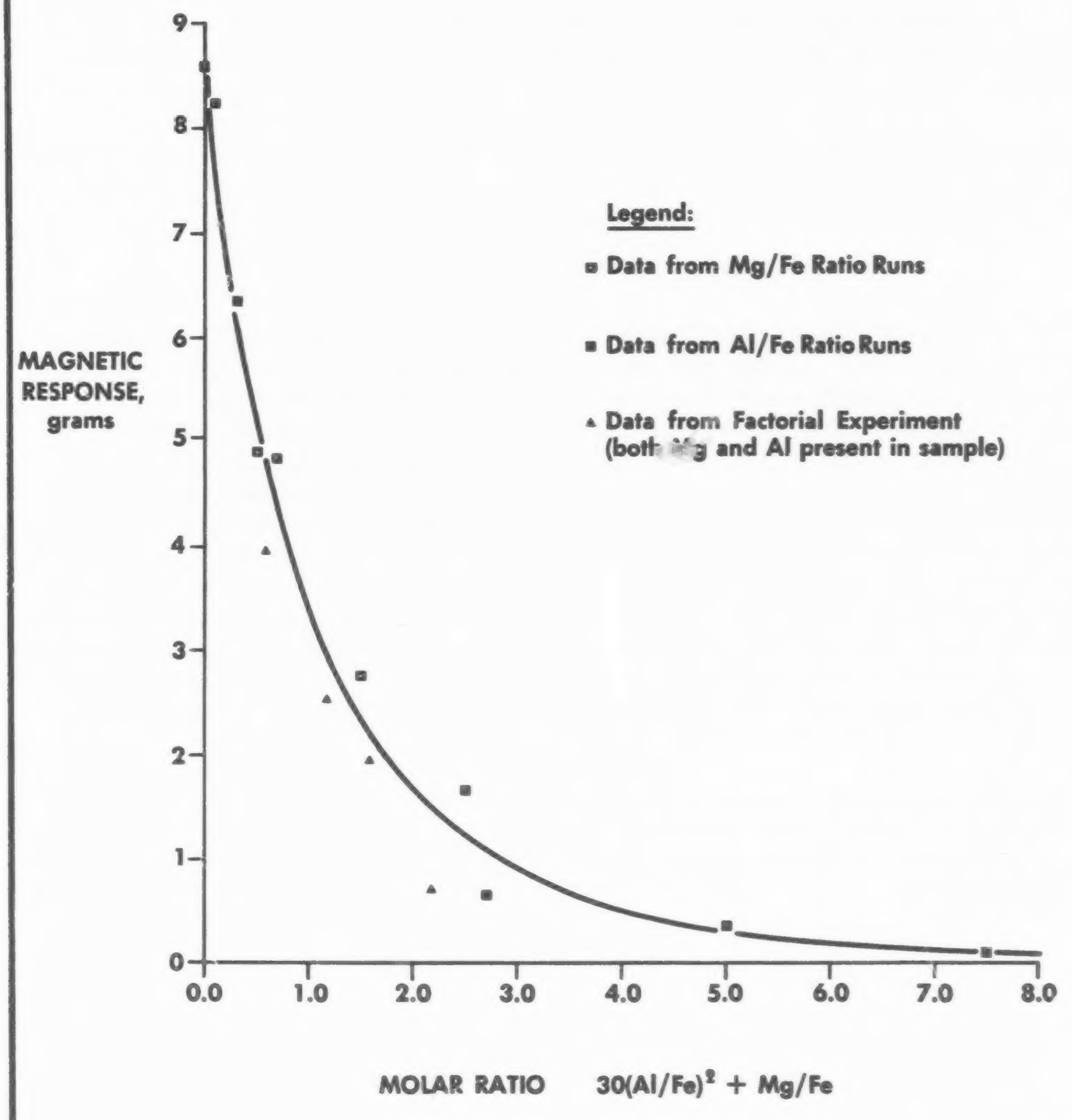

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Figure 6. Variation in Magnetic Response with Increasing Al/Fe and Mg/Fe Molar Ratios

that magnesium interference could be largely eliminated by a preliminary precipitation/sludge separation step. In view of this later finding, therefore, no further attempts were made to verify the validity of the relationships shown above through additional tests with either synthetic or actual coal mine waters.

Magnetic Sludge Seeding Experiments

It was reasoned that the interfering effects of magnesium and aluminum on magnetic sludge formation might be reduced or eliminated, if small amounts of a magnetic sludge were added to the reaction mixture to provide a substrate upon which the freshly formed magnetic sludge could nucleate and grow. This possibility was tested in a series of experiments where small portions of a magnetic sludge, prepared from an actual coal mine discharge, were added to synthetic mine water samples prior to iron precipitation and magnetic sludge formation.

The system chosen for study was that represented by Test 15 of the factorial experiment (Table 5), in which aluminum and magnesium were at their higher levels (corresponding to Al/Fe and Mg/Fe molar ratios of 0.15 and 1.5, respectively). In other words, the effect of the seed material was tested under conditions found by previous experimentation to be definitely inimical to the formation of a strongly magnetic sludge.

The seed material, as noted earlier, was prepared from the Keystone mine water, and was found by emission spectrographic analysis to be essentially free of magnesium and aluminum.

The results of these seeding tests are shown in Table 12. All product sludges were filtered, washed with acetone, dried at room temperature, and weighed. By maintaining weight balances on the sludge and seed material, it was possible to calculate a minimum expected magnetic response based on the assumption that the product material was simply a homogeneous mixture of the seed material and the weakly magnetic sludge produced in the absence of seed material. This calculation also involved the assumption that magnetic response is directly proportional to sample weight, an assumption which was justified by the results of earlier experimental work (see Figure 2). An example of this calculation for Test 397-76 is given below:

TABLE 12. RESULTS OF SEEDING TESTS WITH MAGNETIC SLUDGE FROM KEYSTONE MINE DRAINAGE

Test No.	Wt. Dry Solid Seed Material Added, grams	Magnetic Response of Seed Material, grams		60-Min Settled Sludge Volume Percent**	Sludge Settling Rate, cm/min	Weight of Sludge Obtained, grams		Magnetic Response of 0.200 gram Sludge Sample, grams	
		Actual*	Corrected†			Actual	Minus Wt. of Seed	Actual	Calculated‡
397-71	0.0000	--	--	18.4	0.02	0.8411	0.8411	0.52	--
397-74	0.0500	1.13	1.13	18.4	0.02	0.9110	0.8610	0.35	0.74
397-76	0.1000	2.29	2.26	18.8	0.06	0.9179	0.8179	0.72	0.96
397-80††	0.2000	4.31	4.52	17.3	0.04	1.0033	0.8033	1.45	1.32
397-88#	0.4000	8.48	9.04	18.6	0.02	1.2756	0.8756	1.51	1.78
397-82	0.8000	14.76	18.08	14.2	0.10	1.6539	0.8539	2.45	2.46

* Measured on total amount of seed material used.

† Calculated based on 0.0500 g seed material and assuming direct proportionality between seed sample weight and magnetic response.

** Based on a total suspension volume of 500 ml.

‡ Calculation explained in the text.

†† Averaged data from two tests.

Averaged data from three tests.

Wt. seed material = 0.1000 g

Magnetic Response (M.R.) of 0.0500 g seed material

by actual measurement = 1.13 g

M.R. of 0.1000 g seed material = $\frac{0.1000}{0.0500}$ x 1.13 g = 2.26 g

Wt. sludge formed during reaction = 0.8179 g

M.R. of sludge formed

during reaction[4] = $\frac{0.52}{0.200}$ x 0.8179 = 2.13 g

Combined M.R. of sludge mixture containing 0.1000 g seed plus 0.8179 g fresh sludge = 2.26 + 2.13 = 4.39 g

Calculated M.R. of 0.2000 g sample

of sludge mixture = $\frac{0.2000}{0.9179}$ x 4.39 = 0.96 g

Calculated magnetic responses for 0.200 g portions of the sludge samples from all tests were derived in a similar fashion and are listed in the right-hand column of Table 12.

From a comparison of the calculated and actual (measured) magnetic responses of the product sludges, it seems evident that the presence of the seed material did not result in any appreciable enhancement of magnetic properties of the final sludge. In other words, the data indicate that the product sludge was simply a homogeneous mixture of the original seed material and the weakly magnetic sludge formed in the absence of seed material. This conclusion is supported by the fact that settled sludge volumes remained virtually unchanged until the weight of seed material became so great as to approximate 50 percent by weight of the dried sludge.

The results of these tests, shown graphically in Figure 7, illustrate that the measured magnetic response of the seeded sludge is not much different than that calculated, assuming separate contributions from the seed material and the weakly magnetic, unseeded sludge. A line showing the magnetic response of the seed material alone as a function of sample weight is included in Figure 7 for comparison.

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[4] The measured response of a 0.200 g sludge sample from the unseeded control test (Test 397-71) was 0.52 g.

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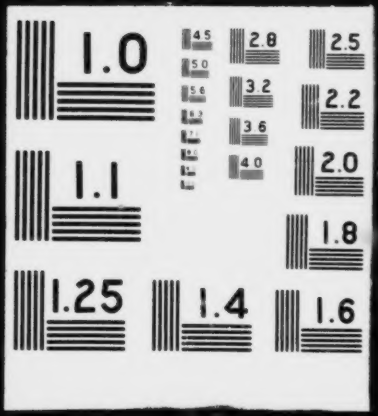
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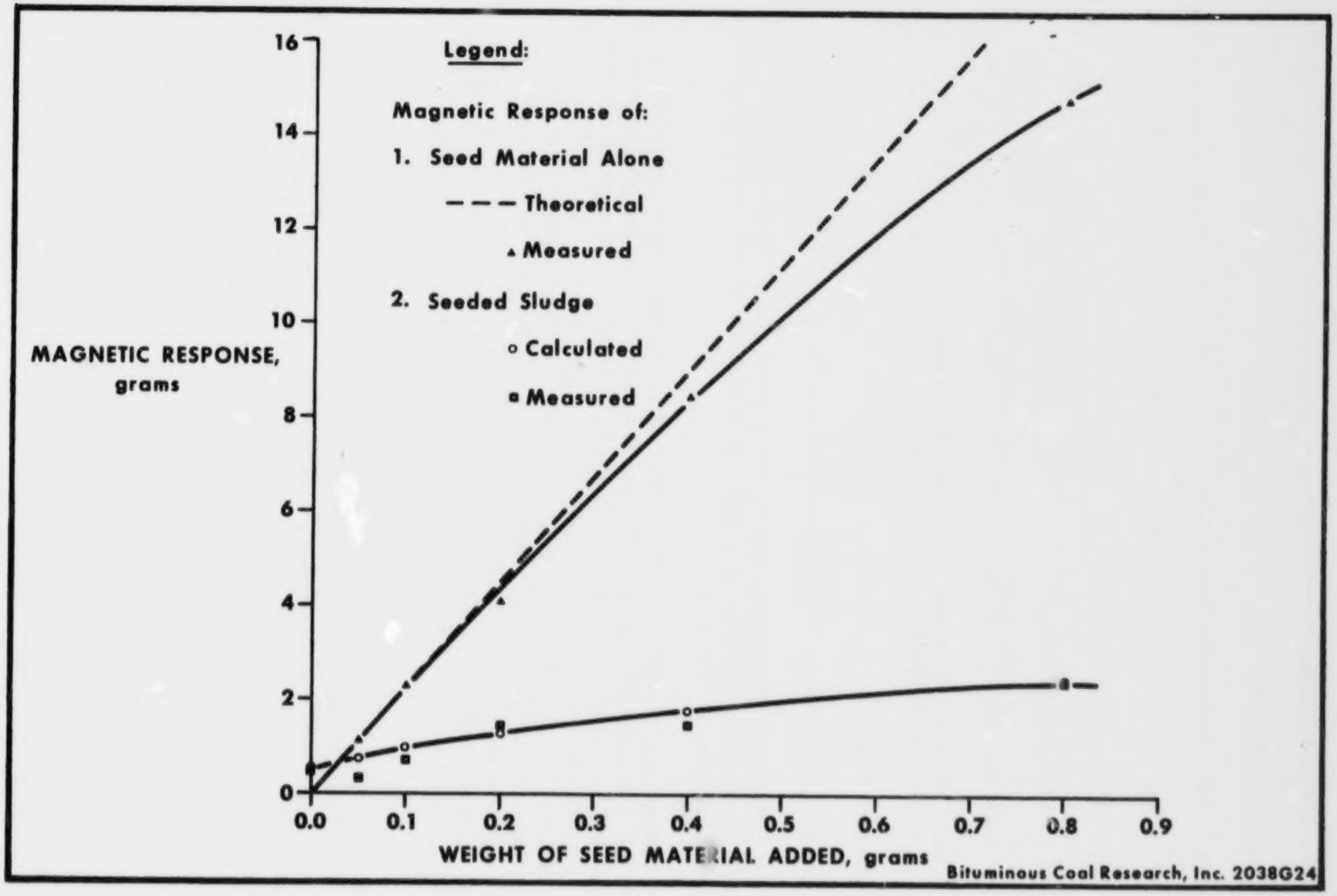

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Figure 7. Results of Seeding Tests with Keystone Magnetic Sludge

Reduction of Magnesium Interference by Preliminary Sludge Concentration

Results of earlier tests (Table 8) showed that even at pH 8, magnesium interference with magnetic sludge formation is still significant; i.e., under conditions where magnesium remains in solution as Mg^{2+}. It was reasoned that this interference might be reduced if the aqueous phase containing Mg^{2+} was separated from the sludge before the magnetic conversion (heating) step.

Initially, a few experiments were conducted using actual coal mine waters from the Keystone and South Greensburg sites (see Table 1). The Mg/Fe and Al/Fe molar ratios in both the raw mine waters and the magnetic sludges prepared therefrom were determined by emission spectrographic analyses. The results of these initial tests are shown in Table 13, and the data show a decided increase in magnetic response when the sludge was concentrated by overnight settling and separated from the supernatant liquid by decantation (Test 397-33). As shown, magnesium was virtually absent from the magnetic sludge product in this case. It is also interesting that in the tests where no prior sludge concentration was employed, about half of the magnesium (and all of the aluminum in the case of Test 397-79) available in the raw mine water reported to the sludge, as indicated by the molar ratios of these impurities with total iron. These results are in agreement with those from the tests with synthetic mine water samples, presented earlier (Tables 9 and 11).

These initial tests were followed by a more extensive series of experiments on the effects of preliminary sludge concentration and separation in reducing magnesium interference during the magnetic sludge conversion step. Tests were conducted using a synthetic mine water solution containing both magnesium and aluminum, and with actual mine drainage samples from the Keystone and Brinkerton sites. As indicated earlier in Table 1, these two actual mine discharges are essentially free of aluminum. Three methods of sludge concentration were employed. The first two involved gravity settling periods for 1 and 16 hours, respectively, followed by decantation of the supernatant liquid. The third method involved a one-hour gravity settling period, followed by decantation of the supernatant liquid, centrifugation of the settled solids, and decantation of the centrate liquid.

The results of these later sludge concentration tests are summarized in Table 14. The data show that protracted settling periods (16 hours) resulted in increases in initial sludge solids contents and decreases in settled sludge volumes, although these changes were generally small in comparison to those obtained by centrifugation of the settled sludge. Conversion of the concentrated sludges to a magnetic form resulted in further increases in solids contents, but with the exception of one possibly anomalous value of 15.8 percent solids for the magnetic sludge obtained from the Brinkerton discharge after preliminary centrifugation (Test 409-30), these increases were of a relatively small order of

TABLE 13. RESULTS FROM INITIAL TESTS ON PRELIMINARY SLUDGE CONCENTRATION

Test No.	Mine Water Sample	Sludge Concentration Method	Molar Ratios†				Sludge Magnetic Response, grams*
			Raw Mine Water		Magnetic Sludge		
			Mg/Fe	Al/Fe	Mg/Fe	Al/Fe	
397-79	1:1 Mixture of Keystone and South Greensburg	None	1.17	0.05	0.51	0.05	0.14
397-77	Keystone	None	0.95	< 0.02	0.57	< 0.02	1.25
397-83	Keystone	None	0.71	< 0.02	0.32	< 0.02	1.44
397-33	Keystone	Overnight Settling	1.07	< 0.02	< 0.02	< 0.02	4.85

† Fe = total iron

* Measured on a 0.200 gram sample of the dried sludge.

TABLE 14. RESULTS OF ADDITIONAL PRELIMINARY SLUDGE CONCENTRATION TESTS DURING MAGNETIC SLUDGE PREPARATION STUDIES

			Concentrated Sludge		Magnetic Sludge					
Test No.	Mine Water Sample*	Sludge Concentration Method†	Weight Percent Solids	Sludge Volume, ml	Weight Percent Solids‡	Sludge Volume, ml‡	Mg/Fe Molar Ratio#	Al/Fe Molar Ratio#	Magnetic Response, Grams	Iron Content, Weight Percent
409-27	Synthetic	A	0.4	876	1.1	392	0.21	0.04	2.31	41.5
409-29	Synthetic	B	1.1	721	1.6	252	0.21	0.04	2.49	47.8
409-25	Synthetic	C	3.8	85	5.0	40	< 0.03	0.04	2.78	42.7
409-40	Keystone	A	1.0	692	3.8	98	< 0.04	≤ 0.02	1.92	31.6
409-37	Keystone	B	1.5	622	5.1	102	< 0.04	≤ 0.02	2.52	29.4
409-18	Keystone	C	6.2	60	6.0	40	< 0.04	≤ 0.02	2.41	30.7
409-32	Brinkerton	A	0.3	651	1.1	134	0.15	≤ 0.04	3.05	27.3
409-34	Brinkerton	B	0.7	471	2.3	101	0.11	≤ 0.04	3.30	25.1
409-30	Brinkerton	C	5.2	35	15.8	10	0.08	≤ 0.04	4.06	32.0

* All tests conducted on 6,000 ml batch samples.

† A - 1 hour gravity settling period.
B - 16 hour gravity settling period.
C - 1 hour gravity settling period followed by centrifugation for 10 min at 1,500 rpm.

‡ Measured after 1 hour gravity settling period.

Molar ratios in raw mine waters:

	Mg/Fe	Al/Fe
Synthetic:	1.53	0.04
Keystone:	0.88	≤ 0.02
Brinkerton:	1.63	≤ 0.04

magnitude. It is perhaps more significant that the one-hour settled sludge volumes of the magnetic sludges were usually less than half those of their nonmagnetic precursors, and in most cases considerably greater reductions in sludge volumes were obtained during the magnetic conversion process.

The most significant results, in terms of the purpose of this study, are reflected by the data for Mg/Fe molar ratios in the magnetic sludges. In all cases the Mg/Fe molar ratios for the sludges are considerably smaller than those for the raw mine waters, indicating that under the experimental conditions most of the magnesium remains in solution and is removed from the sludge during the preliminary sludge concentration-separation step. Consequently, these data support the conclusion that magnesium interference with magnetic sludge formation can be minimized if the initally precipitated (at pH 8.5) ferrous hydroxide sludge is concentrated and separated from the bulk of the mine water before the magnetic sludge conversion. In terms of a practical coal mine drainage treatment process, such a preliminary sludge concentration step has the additional advantage of reducing the volume of that portion of the total flow requiring thermal treatment. These results are in agreement with those obtained during the much earlier exploratory work, where it was observed that preliminary sludge concentration by centrifugation tended to enhance the formation of a magnetic sludge.(1) However, the reasons for this enhancement were not apparent at that time.

The effect of preliminary sludge dewatering on the sludge Mg/Fe molar ratio is probably shown best by the data for the magnetic sludges obtained from the Brinkerton discharge. There is a regular decrease in the Mg/Fe ratio as the method of sludge dewatering becomes more efficient. The results for the Keystone magnetic sludges are more difficult to explain, since the amounts of magnesium in the samples analyzed were consistently below the detectable limit of the method (3 ppm), regardless of the procedure employed for sludge concentration and dewatering.

Composition of Magnetic Sludges Prepared from Actual Coal Mine Waters

It was observed that all of the dried, pulverized magnetic sludges prepared from actual mine waters effervesced strongly when treated with dilute hydrochloric acid. The sludge sample from Test 397-33 (Table 13) was selected for further analytical studies.

X-ray diffraction analysis of this sludge revealed both magnetite (Fe_3O_4) and calcite ($CaCO_3$). Analysis of the sludge by a combustion train procedure for ultimate carbon yielded a value of 4.8 percent carbon, corresponding to approximately 40 percent $CaCO_3$ by weight. This unexpectedly high percentage of calcium carbonate is indicative of the extent of carbonation of the Keystone discharge. In addition, the amount of calcium corresponding to this percentage of $CaCO_3$ is 16.0 percent. Since emission spectrographic analyses revealed that the calcium content of this sludge was 15.4 percent, there is an indication that, for this particular sludge at least, all of the calcium in the sludge is present in the form of $CaCO_3$.

Calcite in those magnetic sludges derived from carbonated mine waters may be considered as an impurity which decreases the bulk magnetic properties of the sludge. This may account for the fact that, in those experiments where the entire mine water samples were heated (Tests 397-79, -77, and -83, Table 13), the data did not fit the relationship developed from similar experiments with synthetic mine waters (Figure 6).

Conceptual Magnetic Sludge Process for Coal Mine Drainage Treatment

Based on the findings discussed above, it is felt that a treatment process for coal mine drainage leading to a magnetic sludge product is technologically feasible under certain conditions. A conceptual process suggested from the results of these studies is presented schematically in Figure 8. The potential usefulness of such a process, as well as the important cost factors involved, will be considered in the following paragraphs.

Process Evaluation

The proposed conceptual magnetic sludge process would be expected to result in the following advantages over existing methods of coal mine drainage treatment:

> Reduced sludge volumes: The data from tests with actual mine waters (Table 14) indicate that approximately five- to seven-fold reductions in settled sludge volumes can be achieved in a magnetic sludge process, compared with sludge volumes obtained by conventional lime treatment. This is further illustrated in Figure 9, which shows the relative volumes of sludges obtained from 1,000-ml batch samples of the Keystone mine water by three different methods of treatment. The magnetic sludge was prepared by heating the solids, previously concentrated by gravity-settling for one hour, at 90 C for 30 minutes. (The material which appears to be in suspension above the magnetic sludge actually consisted of small particles adhering to the inner walls of the Imhoff cone.) Considerably greater reductions in sludge volume may be possible if mechanical dewatering (e.g. centrifugation) is employed during the preliminary sludge concentration step.
>
> Increased solids contents: On the order of four-fold increases in solids contents of the settled sludges were observed to result from the magnetic sludge conversion process. Again, larger increases may be possible with preliminary mechanical dewatering as well as with the use of magnetic separation equipment for final sludge processing.

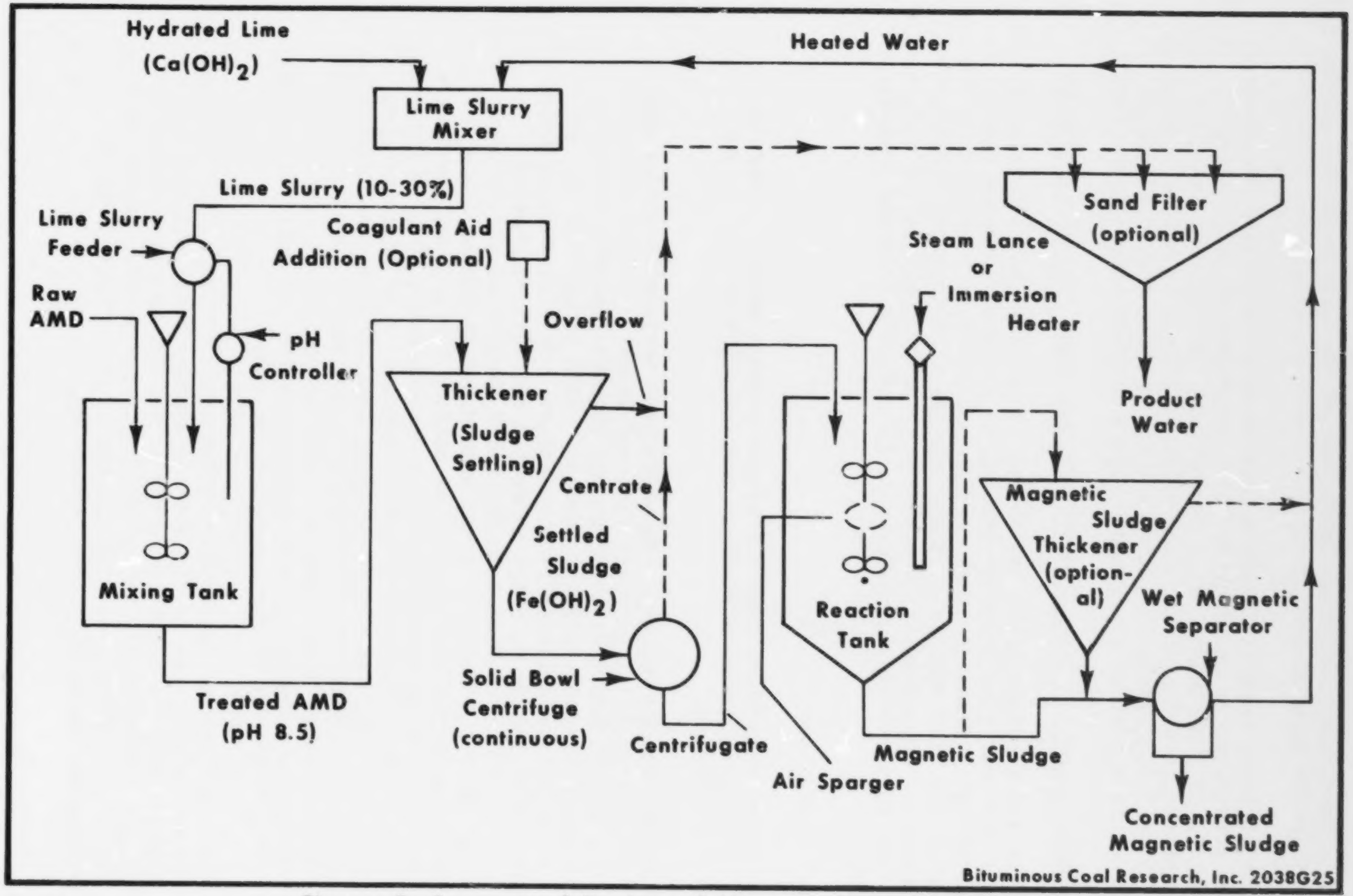
Hydrated Lime
(Ca(OH)2)
Heated Water
Lime Slurry Mixer
Lime Slurry (10-30%)
Lime Slurry Feeder
Coagulant Aid Addition (Optional)
Raw AMD
pH Controller
Overflow
Mixing Tank
Thickener (Sludge Settling)
Centrate
Settled Sludge (Fe(OH)2)
Treated AMD (pH 8.5)
Solid Bowl Centrifuge (continuous)
Centrifugate
Air Sparger
Reaction Tank
Steam Lance or Immersion Heater
Sand Filter (optional)
Product Water
Magnetic Sludge Thickener (option-al)
Wet Magnetic Separator
Magnetic Sludge
Concentrated Magnetic Sludge

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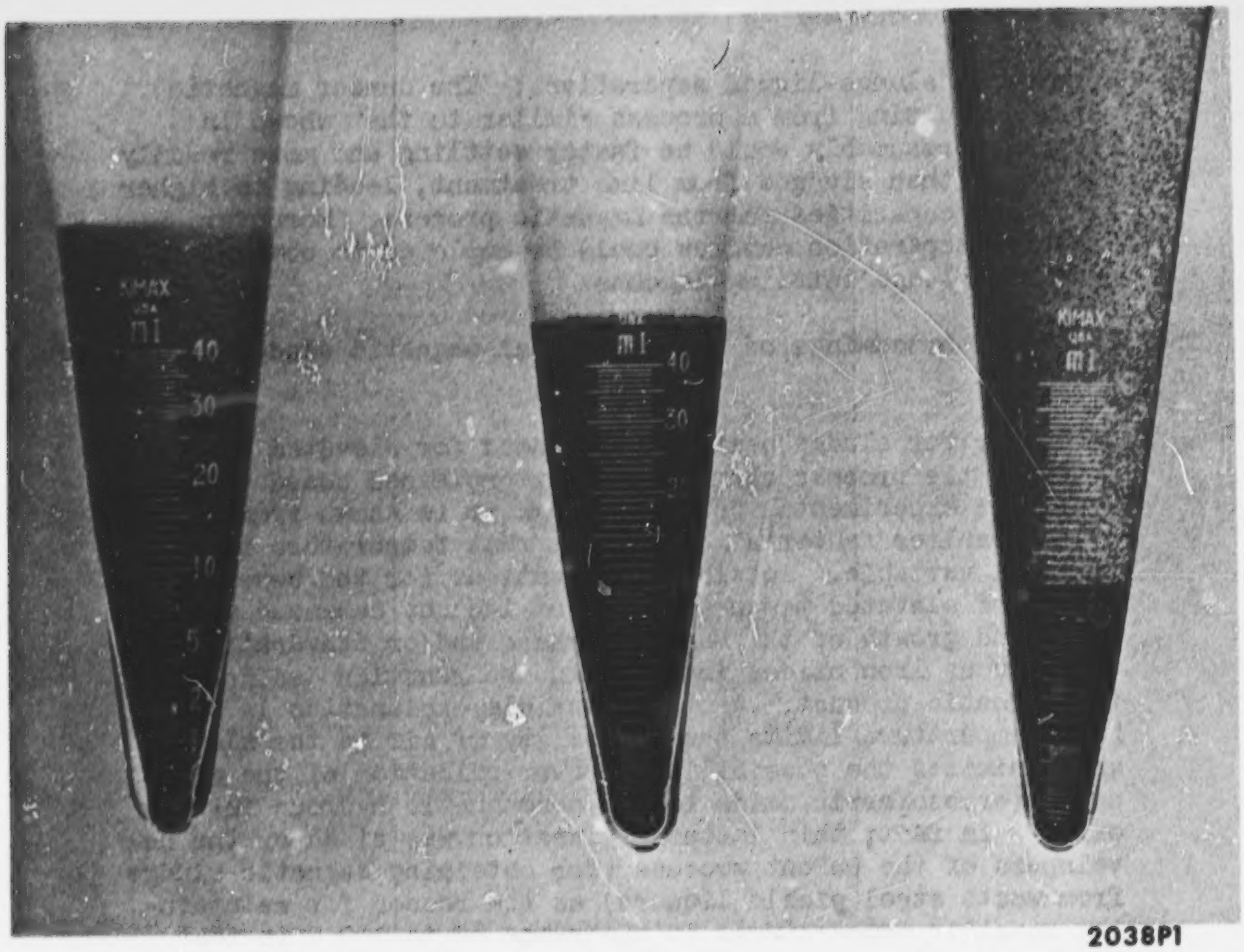
Figure 8. Conceptual Design of Mine Drainage Treatment Process for the Formation of Magnetic Sludge



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Sludge Obtained by Lime Neutralization and Aeration

Sludge Obtained by Lime Neutralization Alone (No Aeration)

Magnetic Sludge

Figure 9. Relative Sludge Volumes After a Thirty Minute Settling Period (Sludges Prepared from Keystone Mine Discharge)

More rapid sludge-liquid separations: The denser magnetic sludge resulting from a process similar to that shown in Figure 8 presumably would be faster settling and more readily dewatered than sludges from lime treatment, leading to higher treatment capacities for the magnetic process. Moreover, magnetic separation devices could be employed to obviate the need for sludge settling lagoons.

The possible shortcomings of the conceptual magnetic sludge process are as follows:

Necessity for sludge heating: The need for elevated temperature in the process cannot be fully explained based on the available experimental data, although it is known from results of the earlier factorial experiment that temperature is a critical variable. Possible explanations for the beneficial effect of elevated temperature might include enhanced nucleation and growth of the magnetic phase and/or dehydration of the hydrous iron oxides involved in the reaction leading to the magnetic product. Another possible explanation is that high temperature limits the solubility of air in the slurry and minimizes the possibility of over-oxidation of the magnetic ferrosoferric oxide to the nonmagnetic hydrous ferric oxide. In fact, this latter explanation was cited by the developers of the DuPont process (for obtaining magnetic sludge from waste steel pickle liquors) as the reason for maintaining reaction temperatures in the range 82 to 100 C in that process.(10)

Close pH control: The necessity to quantitatively precipitate iron, yet avoid coprecipitation of magnesium, imposes relatively tight limitations on pH in the initial neutralization-precipitation step of the treatment process. With modern pH control instrumentation, however, adequate pH control should not prove difficult.

Process restricted to certain types of coal mine waters: Although it has not been stated explicitly before, the magnetic sludge treatment process is presumably limited to those mine waters containing iron principally in the ferrous (Fe^{2+}) state, although theoretically a magnetic product would be possible from a mine water with a Fe^{2+}/total Fe ratio as low as 0.33. Undoubtedly, a more serious limitation is imposed by the sensitivity of the process to aluminum interference, and the fact that many coal mine discharges contain dissolved or suspended aluminum admittedly tends to militate against the practicality of a magnetic sludge process. This matter will be considered further in a subsequent section.

Unfortunately, there does not seem to be any practical way in this application to separate aluminum from iron in solution. The usual procedure in analytical chemistry is to add an excess of a soluble alkali (e.g. NaOH); this causes the aluminum ($Al(OH)_3$) to redissolve as the aluminate ion, AlO_2^-, and the insoluble iron hydroxide remaining is separated by filtration or other means. Such an approach is not feasible in the magnetic sludge process for several reasons, not the least of which is the necessity to avoid coprecipitation of $Mg(OH)_2$ above pH 9.6. It might be possible to keep aluminum in solution near pH 8 through the use of a chelating agent. However, it is doubtful whether any of the known chelating agents are sufficiently specific for aluminum (i.e., iron would also be complexed to some extent), and in any event, use of such materials would probably involve extraordinary conditions and prohibitive costs. Our original concept of controlling the Al/Fe ratio, by blending various mine waters or adding soluble ferrous iron salts, probably offers the most expedient solution to this problem.

Cost Considerations

The conceptual magnetic sludge treatment process might provide the following cost benefits over conventional lime neutralization.

> With the utilization of magnetic separation equipment, costly real estate for sludge settling lagoons would be unnecessary.
>
> Since the process would yield a denser sludge, the cost per unit weight for sludge storage and/or disposal should be reduced.
>
> Heavy-duty aeration equipment of the type commonly used in lime treatment might be replaced with lighter equipment or eliminated altogether.
>
> The magnetic sludge might have some saleable value to offset treatment costs.

On the other hand, certain economic disadvantages are inherent in the magnetic sludge process:

> Reagent (lime) costs would be essentially the same as for conventional lime treatment.
>
> The more sophisticated flowsheet for the process, indicated by Figure 8, suggests that a higher capital investment might be required. In particular, the purchase and installation of specialized equipment such as a continuous centrifuge or magnetic separators would tend to make the process initially more expensive than direct lime neutralization.

The cost of sludge heating would tend to increase operating expenditures. While at first glance the cost of thermal energy for the process might seem to be prohibitive, it may actually be quite reasonable when one realizes that only the sludge itself (which has presumably undergone an initial concentration/dewatering step) and not the bulk of the mine drainage will be heated. For example, in the experiment described earlier involving the preparation of a magnetic sludge for use in seeding experiments, a volume of 2.5 gal of sludge was obtained from an initial 90 gal batch of the Keystone mine drainage after lime treatment and overnight gravity settling. This 2.5 gal of sludge was separated and further processed to yield 0.53 gal of magnetic sludge. By direct proportion, the amount of sludge from the Keystone discharge requiring thermal treatment would be 27.8 gal or 231.8 lb per 1,000 gal of the raw mine water. If it is assumed that the sludge must be heated from 54 F (12 C) to 194 F (90 C), the energy requirement to heat the sludge (assuming the specific heat of the sludge as that of water, i.e. 1 Btu/lb/°F) will be 32,452 Btu. If the average calorific value of bituminous coal is taken as 12,000 Btu/lb, then approximately 3 lb of coal will be consumed per 1,000 gal of raw mine water. If the cost of coal is taken as 0.5¢ per lb, the cost for sludge heating will be about 1.5¢ per 1,000 gal in this particular case. Note that in the example given, no mechanical dewatering (e.g. centrifugation) of the sludge was attempted prior to heating; such practice would have the effect of reducing sludge heating costs even further.

In summary, based on available experimental evidence it would appear that a magnetic sludge treatment process for coal mine drainage is feasible. The limitations of such a process have been defined, and certain restrictions (e.g. magnesium interference) can be minimized through proper process design and control of reaction variables. From a cost standpoint, the magnetic sludge process appears to be competitive with conventional lime neutralization, although a meaningful cost evaluation can only be made after further developmental work on the process.

Amenability of Coal Mine Waters to Magnetic Sludge Treatment

Because of the restrictions involving aluminum contents, many coal mine waters may not be amenable to treatment by a magnetic sludge process. This thought led to a review of two WQO-EPA surveys of coal mine drainage sources within particular watershed areas. Each report contains a considerable amount of tabulated analytical data on the various mine discharges sampled.

The following criteria were used in analyzing the data from these reports: Only those discharges containing 7 ppm or more iron were considered, based on current Pennsylvania stream standards. A mine water was considered treatable by the magnetic sludge process if the Al/Fe molar ratio was 0.18 or less, a value indicated as a practical limit by previous experimental work. A mine water with an Al/Fe molar ratio between 0.19 and 0.26 was considered a borderline case (the value of 0.26 corresponds approximately to the point above which magnetic response decreased sharply with increasing Al/Fe ratios; see Figure 4). Since no data were given on the oxidation state of iron in the mine waters, it was assumed that iron was principally in the ferrous state.

The first report deals with coal mine drainage pollution in the McMahon Creek watershed in Ohio.(11) The McMahon Creek watershed drains 91.2 square miles of Belmont County in southeastern Ohio; McMahon Creek itself, which is "seriously degraded" by mine drainage pollution, flows into the Ohio River at Bellaire, Ohio.

Data on 51 coal mine discharges were tabulated. Of this number, 42 contained $\geq$ 7 ppm iron (one source was not included in the present analysis since no flow data were given). These 42 discharges contained an average iron content of 589.0 ppm Fe (range: 10.3 to 3,228 ppm), an average aluminum content of 90.8 ppm Al (range: 1.0 to 798 ppm), and the average Al/Fe molar ratio was 0.76 (range: 0.01 to 17.06). Eleven of the 42 discharges (26.2 percent) contained less than 100 ppm Fe, and somewhat more remarkable is the fact that 8 of the 42 discharges (19.0 percent) contained more than 1,000 ppm Fe.

The data revealed that 15 of the 42 discharges (35.7 percent) would be treatable by a magnetic sludge process according to the criteria mentioned above, and an additional 3 discharges were borderline cases. Twelve of the 15 treatable discharges are from inactive drift mines, two are from inactive strip mines, and one is from a railroad cut.

The 15 treatable discharges are responsible for 16.6 percent (3,168 lb/day) of the total net acidity load and 40.6 percent (1,671.2 lb/day) of the total iron load contributed by the 42 selected discharges to the McMahon Creek watershed. If the 3 borderline cases are included, these percentages are increased slightly to 17.0 percent and 41.7 percent, respectively.

Seven of the 15 treatable discharges flow directly into McMahon Creek, and represent 68.5 percent (2,684 lb/day) of the total net acidity load and 76.8 percent (1,432.8 lb/day) of the total iron load contributed by all discharges flowing directly into McMahon Creek. Of further interest is the fact that 3 of the 15 treatable discharges are among the 12 "principal mine drainage sources" listed in the report as contributing the largest acidity loadings to the watershed (over 92 percent). These 3 discharges, potentially treatable by a magnetic sludge process, account for only 14.0 percent (2,505 lb/day) of the total net acidity load but 37.1 percent (1,324.0 lb/day) of the iron load attributed to these 12 "principal" discharges.

It was noted from the data that, generally, those discharges with the highest Al/Fe molar ratios were from refuse piles.

The second report reviewed deals with coal mine drainage pollution in the Sewickley Creek watershed in Pennsylvania,(12) and is perhaps more pertinent to the present discussion since some of the sources listed were sampled and utilized routinely during these studies (Table 1). The Sewickley Creek watershed drains 169.0 square miles of Westmoreland County in southwestern Pennsylvania; Sewickley Creek is a major tributary of the Youghiogheny River, which is a tributary to the Monongahela River. Thus, as was the case with McMahon Creek in Ohio, coal mine drainage in the Sewickley Creek watershed utimately flows into the Ohio River.

Data on 61 coal mine discharges were tabulated. Of this number, 48 contained $\geq$ 7 ppm iron (the data from one source with an apparent Al/Fe ratio of 31.3 were rejected as being possibly anomalous). These 48 discharges contained an average iron content of 128.9 ppm Fe (range: 7.9 to 948.0), an average aluminum content of 41.2 ppm Al (range: 1.3 to 147.0 ppm), and the average Al/Fe molar ratio was 1.13 (range: 0.06 to 4.85). Twenty-nine of the 48 discharges (60.4 percent) contained less than 100 ppm Fe

The data revealed that 6 of the 48 discharges (12.5 percent) would be amenable to treatment by a magnetic sludge process, while an additional 3 discharges were borderline cases. One of the borderline cases is a rather large discharge from an active underground mine. The other 2 borderline cases and the 6 potentially treatable cases are all discharges from inactive underground mines of the shaft or drift type.

The 6 treatable discharges are responsible for 37.5 percent (27,278 lb/day) of the total net acidity load and 58.6 percent (13,456 lb/day) of the total iron load contributed by the 48 selected discharges to the Sewickley Creek watershed. If the 3 borderline cases are included, these percentages are increased substantially to 77.2 percent and 89.7 percent, respectively.

It should be noted that of the 10 principal discharges contributing 97.0 percent (70,454 lb/day) of the total net acidity load to the watershed, 3 are treatable and 2 are borderline cases. As a matter of fact, the second and third major discharges in terms of daily acidity loads are, respectively, the Keystone and Brinkerton discharges. Together they contribute 38 percent of the total acid load and 52 percent of the total iron load to the Sewickley Creek watershed. The preparation of dense, strongly magnetic sludges from these two discharges has been successfully demonstrated during the present studies (see, for example, Table 14).

The major findings from this brief literature review are represented schematically in Figure 10. An examination of this pictorial representation will reveal the fallacy of judging the practicality of the magnetic

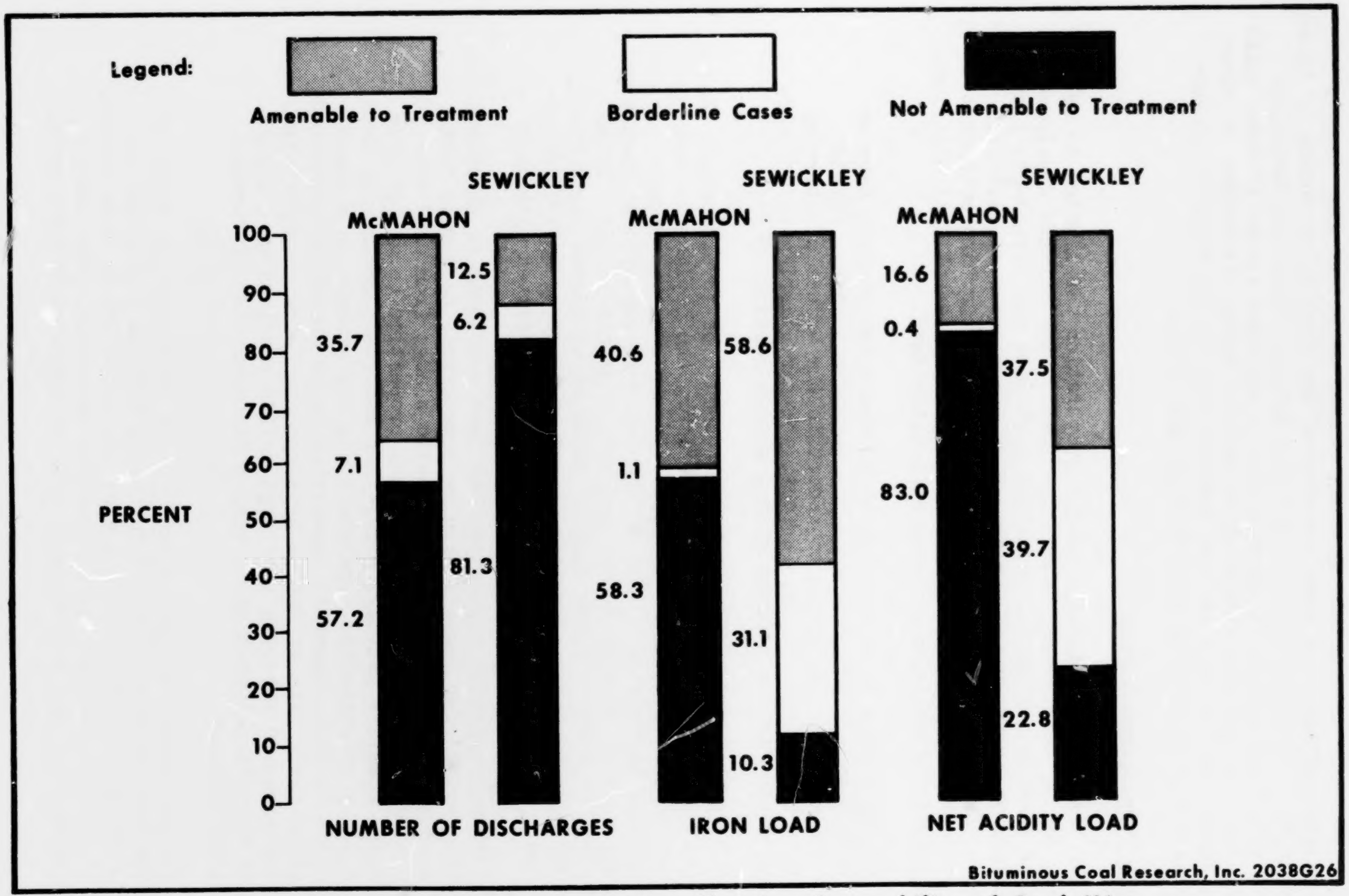

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Figure 10. Schematic Representation Showing Amenability of Coal Mine Discharges from Two Watersheds to Magnetic Sludge Treatment

sludge process based solely upon the number of potentially treatable discharges, without any consideration of the quality or volume of those discharges. Based on the data for the McMahon Creek and Sewickley Creek watershed areas, it appears that a magnetic sludge process would indeed be feasible for treatment of several major discharges in these watersheds, and it is felt that further work on the magnetic sludge process could be readily justified on that basis.

Future Developmental Work

Work in the area of magnetic sludge preparation was limited to relatively small, bench-scale batch experiments, and further developmental work is clearly desirable. Although such work was originally planned, revisions in scope during the course of the program necessitated that these studies be abandoned. Some suggestions regarding optimization of the process conditions are listed below, in the event that additional developmental work is undertaken at a later date.

> Stirring rate is a variable which conceivably could have an effect on the properties of the magnetic sludge. Further work would be desirable to ascertain the effect of stirring rate in the process or, in fact, whether stirring is actually necessary in the process during sludge heating.
>
> The effect of sludge heating time should be investigated. In the DuPont process, mentioned earlier, the optimum heating period was found to be 4 hours. In our own experiments, heating periods of 30 and 60 minutes were employed without any apparent difference in the properties of the sludge. As a first approach, sludge samples could be withdrawn periodically during a protracted heating period and changes in solids content, magnetic response, etc., could be observed with time.
>
> Although magnetic separation has been mentioned as an attractive method for magnetic sludge dewatering, no actual tests were conducted. Since the magnetic sludge from coal mine drainage may have quite different properties (e.g. particle size, specific gravity, etc.) than materials ordinarily handled by wet magnetic separators, as for example in a heavy media circuit, magnetic separation tests should be conducted at an early date if future developmental work is undertaken. The probable increase in sludge solids contents as a result of magnetic separation is also a factor worthy of further investigation.
>
> The procedure for preliminary sludge concentration ahead of the heating step deserves further attention. Although results of some work in this area are contained in this report, it is felt that additional work is necessary. For example, perhaps the use of coagulant aids in conjunction with gravity

settling would prove as good or better than any of the methods tried so far.

The aeration rate, like stirring rate, might influence sludge properties during conversion of the sludge to a magnetic form. Therefore, tests should be conducted to optimize the aeration rate in the process. Aeration during heating may actually not be necessary; in fact, it has been observed in past tests that conversion of the sludge to a magnetic form sometimes occurs readily with heating alone, especially if the sludge has been first concentrated by mechanical dewatering.

Sludge Conditioning Studies

Coagulant Aid Studies

Electrophoretic mobility measurements showed that the sludge particles formed by lime neutralization of the WQO-EPA synthetic coal mine water had an electrostatic charge of +17 to +25 millivolts. Therefore, the use of anionic coagulant aids was indicated. The objective in coagulant aid addition is to add just enough of the coagulant to reduce the electrostatic forces of mutual repulsion to a minimum, i.e., to or near a value of zero (the isoelectric point). When this is accomplished, the particles are more susceptible to agglomeration and tend to settle more rapidly. It was thought that this more rapid settling, together with the possibility of greater sludge compaction, might result in the formation of a denser sludge after settling.

In these studies, 12 anionic polyelectrolytes and 2 nonionic polyelectrolytes were tested. These coagulant aids are representative of the type commercially available today. The coagulant aids tested are listed in Table 15, which also shows the concentration of each coagulant aid necessary to achieve the isoelectric point. Six of the anionic polyelectrolytes were effective at concentrations below 1 ppm. The zeta potential curves for these six most effective coagulant aids are shown in Figure 11. Another group of five coagulant aids were effective within the concentration range 1 to 5 ppm, and results with these samples are shown in Figure 12. Although the curves in Figures 11 and 12 would indicate that charge reversal should be effected by further increased concentrations of the coagulant aids, it was actually found for nearly all coagulant aids tested that further additions up to the 20 ppm level did not affect the apparent sludge zeta potential, i.e., it remained at zero.

Zeta Floc WA is rather unique in that, in addition to containing a "strongly anionic" polyelectrolyte, it also contains an appreciable percentage of insoluble aluminum silicate as a bulk additive. On a weight-for-weight basis, therefore, one would expect that a substantially larger amount of this coagulant aid would be required to achieve the isoelectric point compared with the other anionic coagulant aids

TABLE 15. EFFECT OF COAGULANT AIDS ON SLUDGE FROM LIME TREATMENT OF WQO-EPA SYNTHETIC COAL MINE WATER

Additive	Source	Concentration at Isoelectric Point, ppm
Magnifloc 836A	American Cyanamid Co., Industrial Chemicals Division	0.1
Magnifloc 837A	American Cyanamid Co., Industrial Chemicals Division	0.5
Polyfloc 1130	Betz Laboratories, Inc.	0.6
Magnifloc 835A	American Cyanamid Co., Industrial Chemicals Division	0.7
Genfloc 155	General Mills, Inc.	0.7
Superfloc 16	American Cyanamid Co., Industrial Chemicals Division	0.8
Nalcolyte 673	Nalco Chemical Co.	1.0
Calgon 240	Calgon Corporation	1.0
Polyhall M-295	Stein, Hall & Co., Inc.	1.5
Reten AM	Hercules, Inc.	2.0
Primafloc A-10	Rohm & Haas Co.	5.0
Zeta Floc WA‡	Narvon Mining & Chemical Co.	40
Superfloc 127†	American Cyanamid Co., Industrial Chemicals Division	*
Polyox WSR-301†	Union Carbide Corp., Chemicals Division	*

‡ Contains insoluble aluminum silicate.

† Nonionic polyelectrolyte - all other coagulant aids are anionic polyelectrolytes.

* Isoelectric point never achieved; sludge remained electropositive.

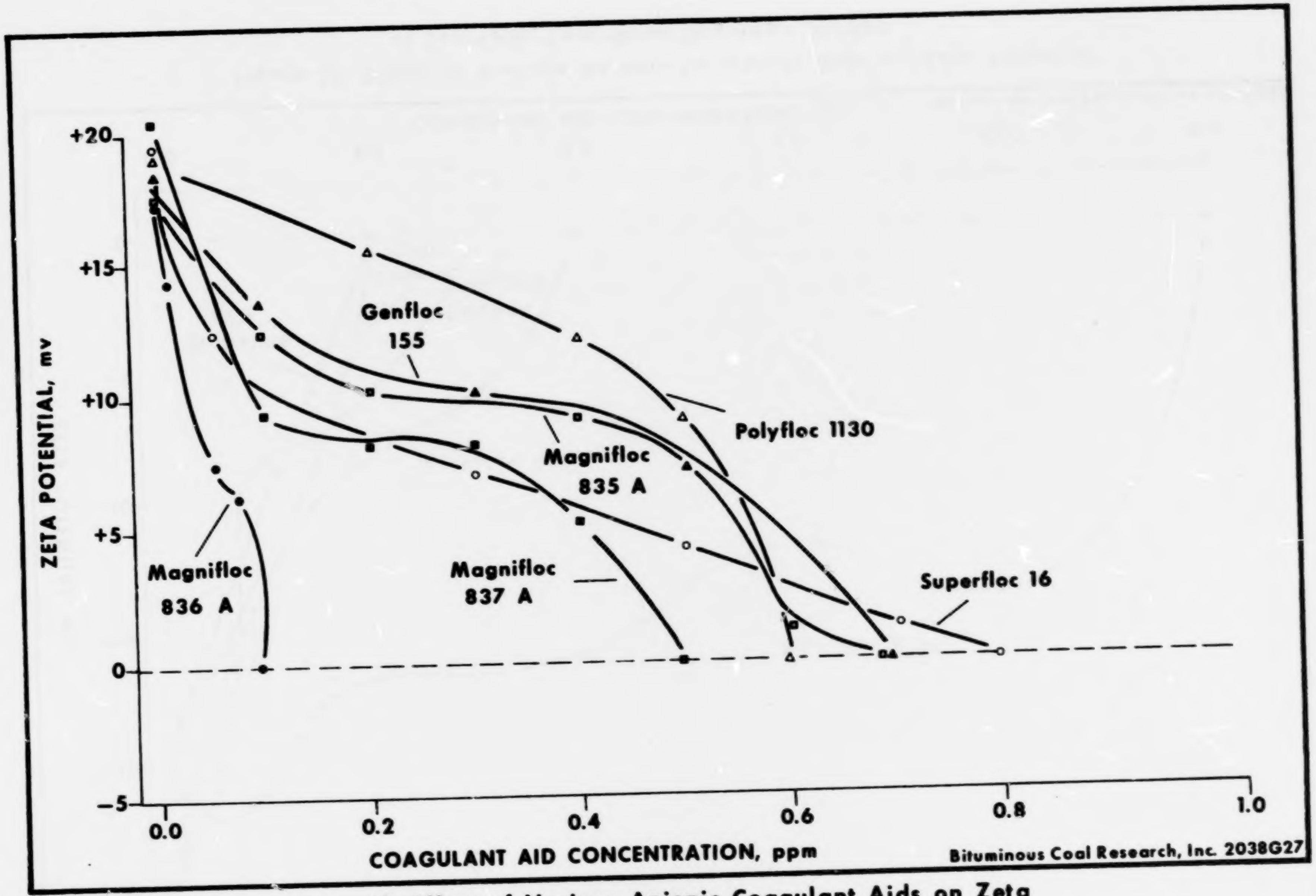

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Figure 11. Effect of Various Anionic Coagulant Aids on Zeta Potential of Synthetic Coal Mine Drainage Sludge

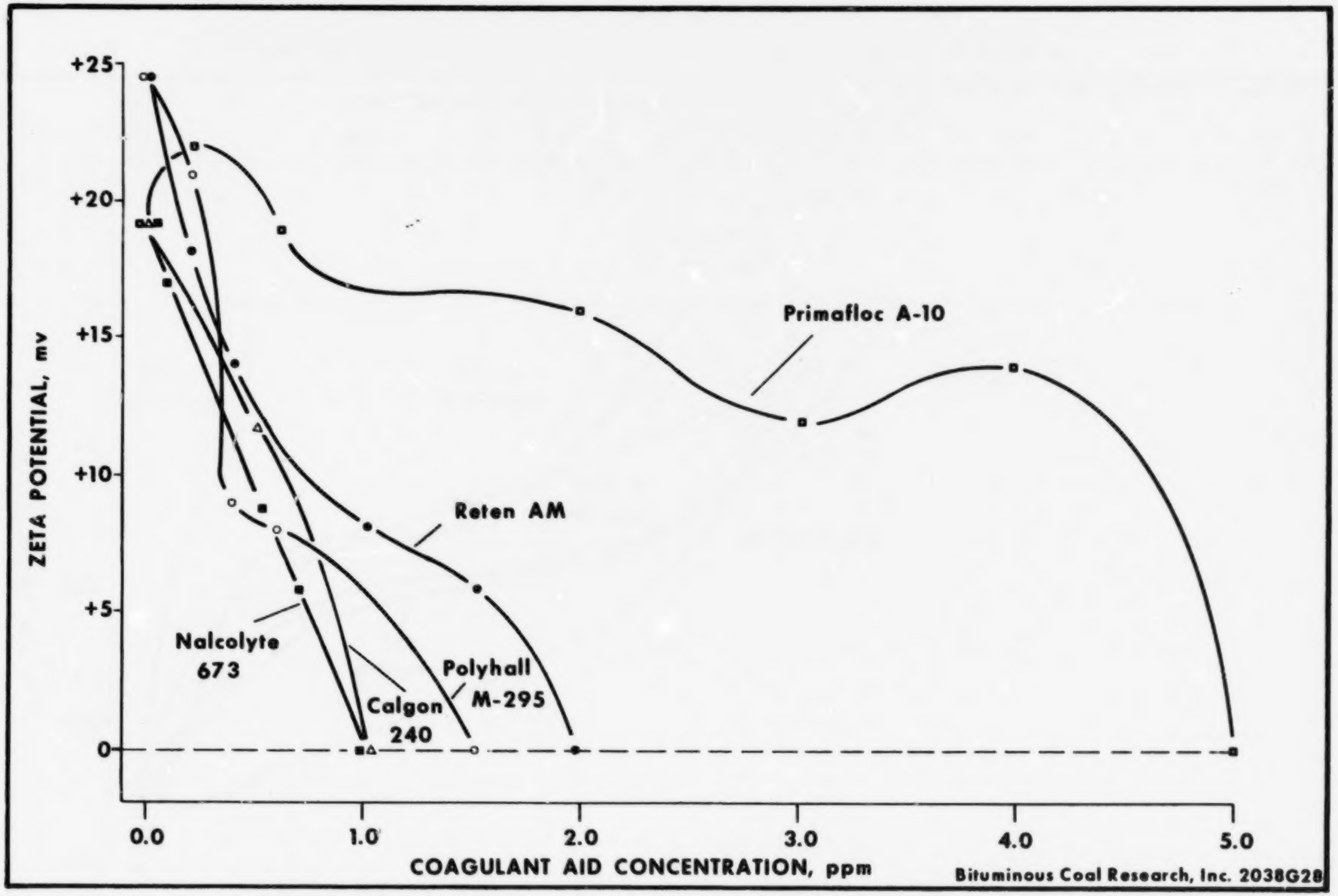

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Figure 12. Effect of Various Anionic Coagulant Aids on Zeta Potential of Synthetic Coal Mine Drainage Sludge

tested, and this is borne out by the results, shown in Figure 13. On the other hand, according to the manufacturer's literature, competitive polyelectrolytes "generally sell for ten to twenty times as much as Zeta Floc on a cost per pound basis." On this basis, therefore, Zeta Floc WA could probably be considered comparable in efficiency with those coagulant aids whose zeta potential curves are shown in Figure 12.

As expected, the isoelectric point was not achieved using the two nonionic polyelectrolytes, Superfloc 127 and Polyox WSR-301, as indicated by Figure 14. Relatively large dosages ($\geq$ 50 ppm) appeared to result in a stable zeta potential in the range +7 to +9 millivolts.

The effects of coagulant aids alone on settling rates, sludge volumes, and solids contents of the sludge obtained by lime neutralization of the WQO-EPA synthetic water are shown by the data in Table 16. These results indicate that in practically every instance, sludge settling rates increased as the coagulant aid dosage was increased. This effect was especially pronounced when a relatively large excess of the coagulant aid (e.g. 20 ppm) was employed. These settling rate increases were also accompanied by marked improvements in the clarity of the supernatant liquid, as reflected by the data on turbidity. The one exception in these tests was the nonionic Polyox WSR-301, which failed to effect any appreciable changes in sludge settling rate or supernatant liquid turbidity up to a dosage of 100 ppm. Use of the other nonionic coagulant aid, Superfloc 127, led to results quite similar to those obtained with the anionic polyelectrolytes.

When the anionic polyelectrolytes were employed at the minimum concentrations necessary to achieve the isoelectric point (see Table 15), the fastest settling was obtained with Genfloc 155, while three coagulant aids (Polyfloc 1130, Genfloc 155, and Nalcolyte 673) resulted in minimum turbidity values of 3 JTU. However, the data are characterized more by similarities than by differences, and where differences do appear they are often so small as to be within the limits of experimental error. Thus, it should be emphasized that these results do not imply an endorsement for any particular coagulant aid, and any such judgment should be predicated on a much more exhaustive series of flocculation tests under conditions more closely approaching those used in actual plant practice. At best, our data indicate that there are not significantly large differences among the results obtained with the various anionic polyelectrolytes tested; in addition, the data suggest that the use of excess amounts of the coagulant aids (i.e., dosages above the minimum necessary to achieve the isoelectric point) is desirable, and the additional reagent cost thereby incurred might be justified on the basis of substantially improved results.

Slight increases in 30-minute settled sludge volumes were observed with increasing coagulant aid dosages. This result is quite likely due to the fact that a greater proportion of the suspended solids were settled in the presence of the coagulant aids.

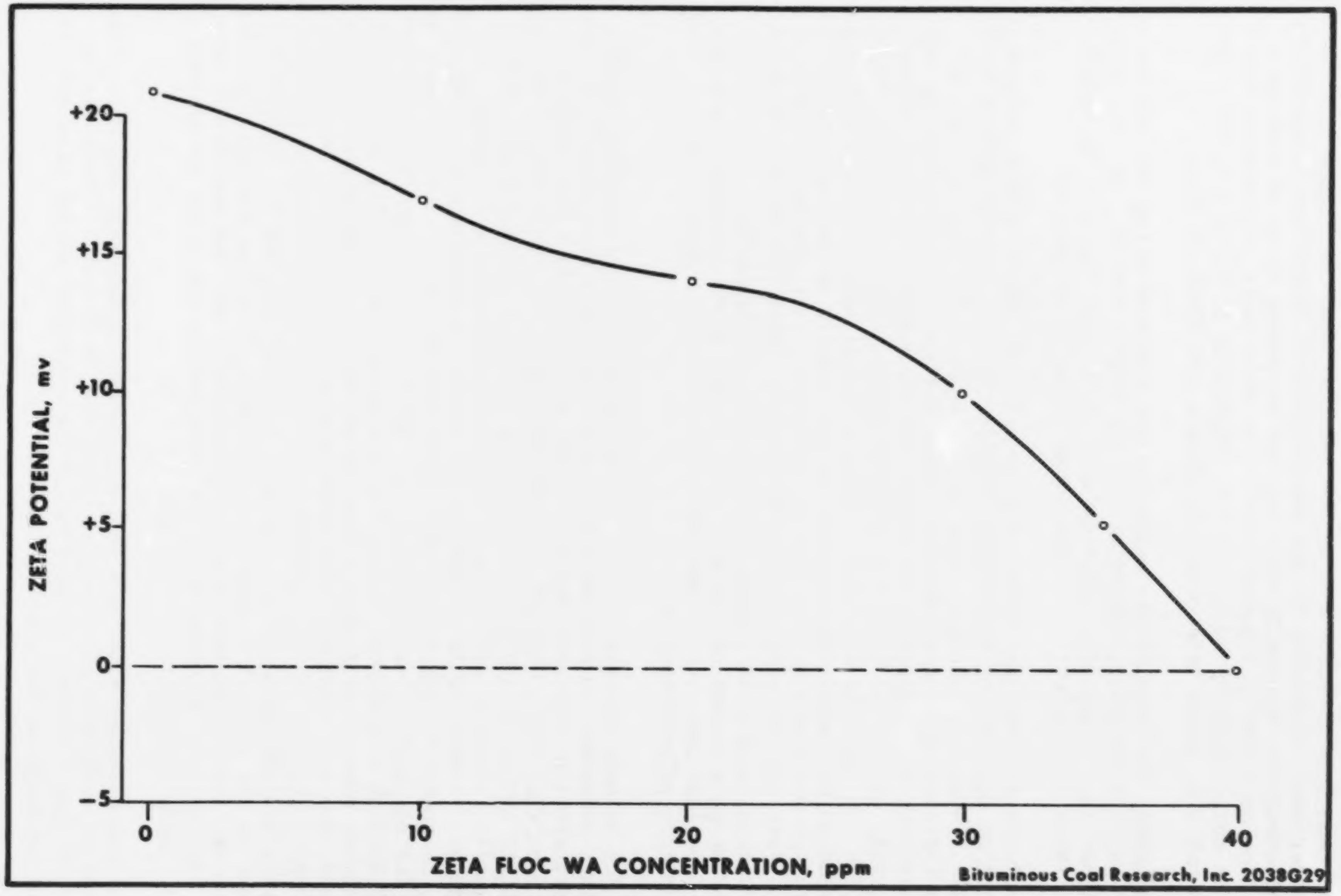

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Figure 13. Effect of Zeta Floc WA on Zeta Potential of Synthetic Coal Mine Drainage Sludge

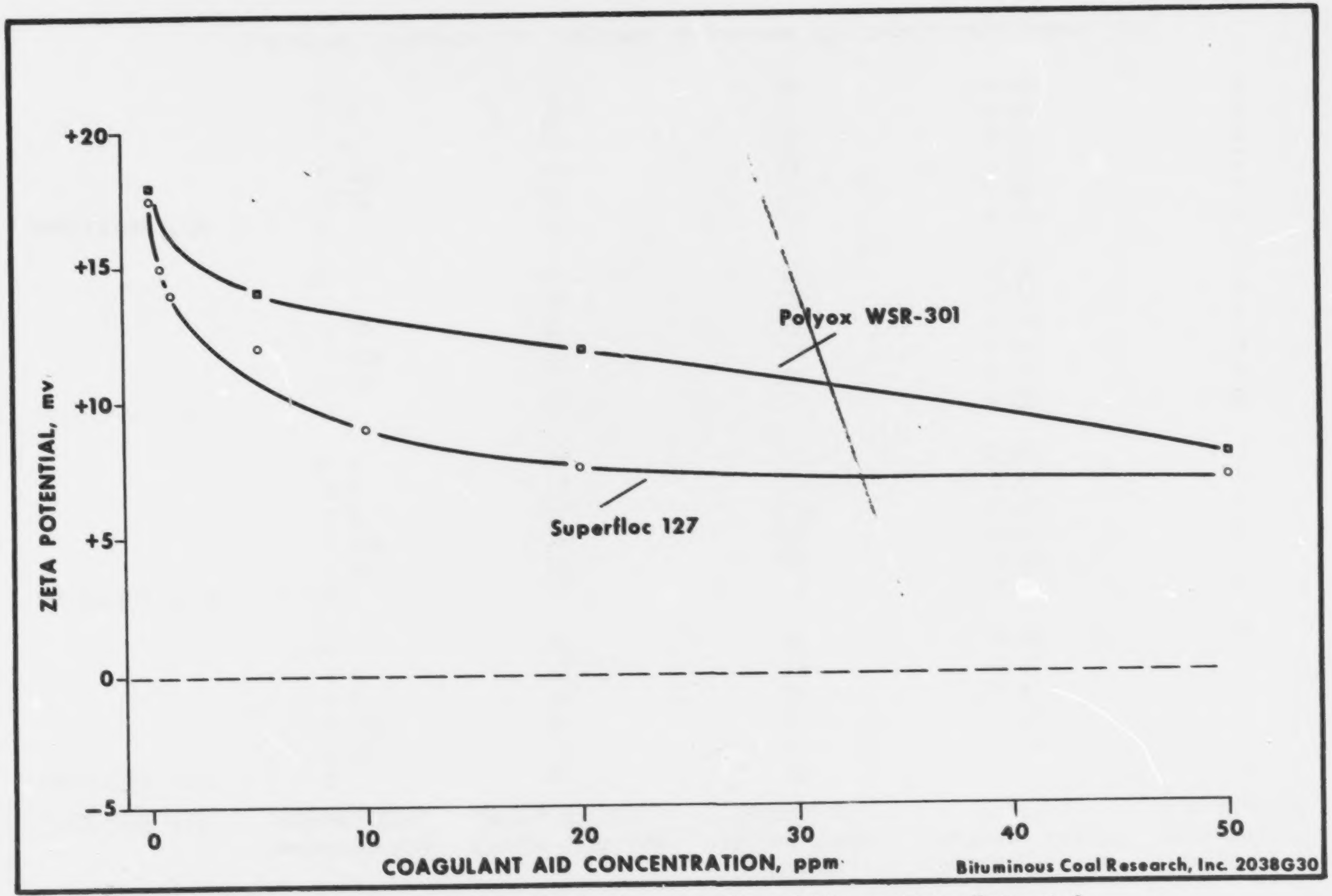

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Figure 14. Effect of Two Nonionic Coagulant Aids on Zeta Potential of Synthetic Coal Mine Drainage Sludge

TABLE 16. EFFECTS OF COAGULANT AIDS ON SETTLING RATES, SLUDGE VOLUMES, AND SOLID CONTENTS OF SYNTHETIC COAL MINE WATER SLUDGE

Coagulant Aid	Coagulant Aid Dosage, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
Magnifloc 836A	0	19	14	0.40	15
	0.05	28	14	0.45	8
	0.10*	40	14	0.51	8
	1.0	49	17	0.47	3
	5.0	71	19	0.53	3
	20.0	78	20	0.45	1
Magnifloc 837A	0	19	13	0.37	17
	0.30	28	14	0.39	5
	0.50*	36	14	0.43	6
	1.0	41	14	0.41	2
	5.0	78	17	0.44	2
	20.0	84	17	0.33	1
Polyfloc 1130	0	19	15	0.53	18
	0.50	33	16	0.44	4
	0.60*	33	18	0.47	3
	0.80	33	18	0.49	2
	1.0	34	18	0.37	2
	20.0	98	17	0.54	2
Magnifloc 835A	0	19	14	0.49	21
	0.20	28	13	0.50	6
	0.70*	49	13	0.39	5
	1.0	57	14	0.41	3
	5.0	78	17	0.49	5
	20.0	84	16	0.41	3

* Minimum concentration required to achieve the isoelectric point.

TABLE 16. EFFECTS OF COAGULANT AIDS ON SETTLING RATES, SLUDGE VOLUMES, AND SOLID CONTENTS OF SYNTHETIC COAL MINE WATER SLUDGE (Cont.)

Coagulant Aid	Coagulant Aid Dosage, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
Genfloc 155	0	18	14	0.61	18
	0.30	52	16	0.47	3
	0.70*	63	17	0.29	3
	1.0	63	17	0.41	2
	5.0	75	18	0.43	2
	20.0	78	17	0.31	6
Superfloc 16	0	20	14	0.44	18
	0.50	33	14	0.58	6
	0.80*	43	11	0.76	11
	1.0	40	14	0.55	4
	5.0	79	15	0.70	4
	20.0	79	15	0.82	6
Nalcolyte 673	0	20	13	0.20	16
	0.50	33	15	0.27	5
	1.0*	45	15	0.35	3
	3.0	69	17	0.29	2
	5.0	71	19	0.25	3
	20.0	79	19	0.32	2
Calgon 240	0	20	14	0.38	17
	0.50	30	13	0.55	7
	1.0*	32	16	0.52	5
	3.0	38	16	0.52	2
	5.0	39	16	0.59	2
	20.0	77	16	0.76	3

* Minimum concentration required to achieve the isoelectric point.

TABLE 16. EFFECTS OF COAGULANT AIDS ON SETTLING RATES, SLUDGE VOLUMES, AND SOLID CONTENTS OF SYNTHETIC COAL MINE WATER SLUDGE (Cont.)

Coagulant Aid	Coagulant Aid Dosage, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
Polyhall M-295	0	21	14	0.36	21
	0.50	27	14	0.40	4
	1.5*	33	15	0.33	4
	3.0	56	16	0.36	2
	5.0	59	17	0.57	3
	20.0	65	17	0.39	2
Reten AM	0	22	15	0.30	16
	1.0	35	15	0.32	2
	2.0*	60	15	0.25	5
	3.0	69	16	0.32	1
	5.0	61	16	0.85	4
	20.0	80	17	0.45	1
Primafloc A-10	0	20	14	0.55	23
	1.0	22	15	0.51	16
	3.0	30	15	0.68	12
	5.0*	30	15	0.69	9
	10.0	43	16	0.62	8
	20.0	41	17	0.68	7
Zeta Floc WA	0	23	14	0.35	16
	10.0	28	14	0.21	5
	20.0	34	14	0.34	4
	30.0	34	15	0.46	3
	40.0*	37	15	0.44	4
	50.0	37	16	0.36	4

* Minimum concentration required to achieve the isoelectric point.

TABLE 16. EFFECTS OF COAGULANT AIDS ON SETTLING RATES, SLUDGE VOLUMES, AND SOLID CONTENTS OF SYNTHETIC COAL MINE WATER SLUDGE (Cont.)

Coagulant Aid	Coagulant Aid Dosage, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
Superfloc 127	0	20	13	0.51	22
	0.10	34	13	0.36	10
	0.50	39	13	0.40	6
	1.0	69	13	0.25	6
	5.0	81	15	0.41	4
	20.0	85	12	0.64	3
Polyox WSR-301	0	21	13	0.64	31
	3.0	24	13	0.60	28
	5.0	24	13	0.47	26
	20.0	29	13	0.43	16
	50.0	25	13	0.40	24
	100.0	26	13	0.55	28

With regard to sludge solids contents, there is some indication of a trend toward slightly higher solids contents with increasing coagulant aid dosage. However, it is felt that such an effect is negligible, if present at all. This is apparent when one considers the solids content data for the control samples to which no coagulant aid was added. These values range from a low of 0.20 percent solids to a high of 0.64 percent solids, with a mean deviation of 0.10. Since practically all of the values determined (with and without coagulant aids) lie within this range, it is evident that no significant increases in sludge solids contents were obtained through the use of coagulant aids. In summary, then, the combined data on sludge volumes and solids contents indicate that the use of coagulant aids alone will not result in increases in sludge density.

Filter Aid Studies

The purpose of this series of tests was to determine whether or not sludge density could be increased significantly by the addition of various bulk additives or sludge "builders." These materials might also be of use as filtration aids, affording more rapid and efficient sludge dewatering.

The materials tested are listed in Table 17. Results of preliminary tests with the fly ash indicated slightly increased settling rates and decreased turbidity when the filter aid was added to the synthetic mine water before rather than after the lime, during sludge preparation. Results of a previous BCR study (1) on the use of coagulant aids with a ferrous hydroxide sludge indicated a slight advantage was gained in terms of a lower coagulant aid requirement when the fly ash was added before the lime. This earlier study also involved tests with fly ash (and other "inert solids") in combination with Calgon 240, and for the sake of comparison with these previous results, Calgon 240 was likewise chosen for use in the present studies.

Preliminary electrophoretic mobility measurements indicated that the presence of fly ash alone had a somewhat erratic effect on the zeta potential of the sludge prepared by lime treatment of the WQO-EPA synthetic mine water, although there was a general tendency for the sludge zeta potential to decrease as the amount of fly ash added was increased. Relatively high concentrations of fly ash, on the order of 2 to 5 grams per liter, were required to lower the zeta potential of the sludge to the isoelectric point.

The results of tests using the filter aids alone are shown in Table 18. The data reveal that as the amount of filter aid added to the suspension was increased, there was an increase in sludge solids contents and a decrease in settled sludge volume in practically all cases, indicating that an overall increase in sludge density had been effected. In addition, sludge settling rates were increased by a factor of about 1.5 to 2 over those measured in the absence of the filter aids (Table 16).

TABLE 17. MATERIALS USED IN FILTER AID STUDIES

Filter Aid	Source	Density,* g/ml	Remarks
Fly ash	Colfax Power Station Duquesne Light Co.	2.29	Sieved as received to minus 200 mesh.
Blast furnace slag (agricultural grade)	U.S. Steel Corp. Duquesne Works	2.81	Dried at 105 C, ground and sieved to minus 200 mesh.
Magnetite (heavy media grade)	Mineral Mills, Inc., "Floatkleen," Grade 6	5.10	Used as received, 98+ percent minus 200 mesh.
Sawdust	Rosensteele and Kunkle Co., Spring Church, Pa.	1.47	Sieved as received from saw mill to minus 20 mesh.
Gypsum	Fisher Scientific Co.	2.42	Reagent grade $CaSO_4 \cdot 2H_2O$ powder, used as received.
Sand	Rosensteele and Kunkle Co., Spring Church, Pa.	2.83	Dried at 105 C, ground and sieved to minus 200 mesh.
"Red Dog"	Sewickley Township Westmoreland County, Pa.	2.75	Product of coal refuse combustion; ground and sieved to minus 200 mesh.
Magnetite (pigment grade)	Columbian Carbon Division, Cities Service Co. Mapico Black, Lot 1296	5.62	Used as received, 99.9 percent minus 325 mesh (predominant particle size range 0.2 to 0.8 microns).

* Determined with a Beckman Model 930 Air Comparison Pycnometer.

TABLE 18. EFFECTS OF FILTER AIDS ALONE ON PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

Filter Aid	Filter Aid Dosage, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Sludge Zeta Potential, mv	Turbidity of Supernatant Liquid, JTU
Fly ash	500	45	11	1.22	+ 11	24
	2,000	45	9	3.23	+ 16	32
	5,000	40	8	6.82	0	37
Slag	500	29	16	0.91	+ 12	27
	2,000	35	12	1.88	+ 13	35
	5,000	43	8	7.21	+ 13	36
Magnetite (heavy media grade)	500	35	11	0.94	+ 14	27
	2,000	30	8	4.42	+ 17	42
	5,000	35	7	8.50	+ 13	41
Sawdust	500	45	12	0.70	+ 13	26
	2,000	40	12	0.93	+ 16	24
	5,000	47	14	2.34	+ 17	24
Gypsum	500	30	12	0.68	+ 18	22
	2,000	32	12	1.44	+ 17	18
	5,000	35	8	5.78	+ 1	12
Sand	500	26	12	1.07	+ 12	19
	2,000	28	10	1.72	+ 12	32
	5,000	29	9	3.82	+ 12	33
"Red Dog"	500	27	10	1.80	+ 11	27
	2,000	28	10	3.30	+ 15	29
	5,000	29	9	6.32	+ 17	35
Magnetite (pigment grade)	500	32	12	1.13	+ 29*	34
	2,000	38	10	2.90	+ 23*	31
	5,000	33	9	5.66	+ 24*	19

* Presence of the filter aid apparently interfered with electrophoretic mobility measurements, and values may be anomalous.

On the other hand, turbidity data indicate that an appreciable amount of material remained in suspension after the 30-minute settling period. The data on sludge zeta potential indicate that the electrophoretic mobility of the sludge was affected in a rather erratic and inconsistent way in the presence of the filter aids alone. Only the fly ash and gypsum seemed to have a definite lowering effect on the sludge zeta potential at the highest concentrations employed (5,000 ppm).

The results of tests using the filter aids in conjunction with 0.5 ppm of the anionic polyelectrolyte Calgon 240 are shown in Table 19. As expected, use of the coagulant aid resulted in further increases in sludge settling rates and decreases in supernatant liquid turbidity, compared with the results of the same tests where the coagulant aid was absent (Table 18). In addition, it is significant that the isoelectric point was achieved in nearly all cases with 0.5 ppm of Calgon 240. This is only one-half the amount that was required in the absence of the filter aids (Table 15). Thus, there is evidence that for a given concentration of the coagulant aid, the combination of the filter aid and coagulant aid has a more pronounced effect on the sludge zeta potential than does the coagulant aid alone. This finding is in agreement with that reported previously,(1) however, similar tests with other coagulant aids would be necessary to establish whether it applies generally in all cases.

In view of the settling rate data from tests with Calgon 240 alone (Table 16), it is felt that the filter aid-Calgon 240 combination resulted in significant increases in sludge settling rate. With regard to settled sludge volumes and solids contents, the differences between the results with filter aids alone and with the filter aid-coagulant aid combination are not sufficiently large to be meaningful.

The effects of the filter aids alone on sludge solids contents are illustrated graphically in Figure 15. The curves show a generally regular increase in solids contents with increasing filter aid concentration for most of the materials evaluated. The two notable exceptions are the curves for gypsum and blast furnace slag; it is apparent that the increases in sludge solids contents become comparatively larger as the concentrations of these two materials increase. The role of gypsum in promoting coal mine drainage sludge densification has been implied by a number of workers, and the presence of gypsum seed crystals has been suggested as the factor responsible for the effectiveness of sludge densification by recycling techniques.(13) In addition, rather striking evidence of the effects of coprecipitated gypsum on sludge density was observed during the magnetic sludge studies (for example, see Figure 3). Thus, it is perhaps not surprising that results of the present studies indicate that gypsum is an effective sludge densifier. The other material which appears to be effective, blast furnace slag, has to our knowledge not been employed previously in an application of this type. Our results suggest that its use should be further explored, particularly since it is a relatively cheap waste product which also contains a reactive alkaline component (see below).

TABLE 19. EFFECTS OF FILTER AIDS PLUS 0.5 PPM CALGON 240 ON PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

Filter Aid	Filter Aid Dosage, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Sludge Zeta Potential, mv	Turbidity of Supernatant Liquid, JTU
Fly ash	500	52	11	1.11	+ 7	8
	2,000	48	9	3.20	0	16
	5,000	60	8	6.64	0	12
Slag	500	26	16	0.87	0	14
	2,000	56	11	2.43	+ 1	17
	5,000	59	8	6.53	+ 10	25
Magnetite (heavy media grade)	500	48	10	1.15	+ 10	12
	2,000	65	7	4.31	+ 1	25
	5,000	90	7	8.60	+ 1	11
Sawdust	500	65	12	0.68	+ 1	13
	2,000	63	12	0.90	+ 1	8
	5,000	70	13	2.47	0	11
Gypsum	500	38	12	0.64	+ 1	10
	2,000	55	11	1.40	+ 1	10
	5,000	60	8	4.86	0	8
Sand	500	35	12	1.26	0	11
	2,000	43	9	2.46	0	12
	5,000	50	9	6.29	0	19
"Red Dog"	500	35	10	1.60	0	16
	2,000	42	10	3.18	0	14
	5,000	65	9	6.70	0	15
Magnetite (pigment grade)	500	37	11	1.13	+ 12*	20
	2,000	43	8	2.91	+ 24*	17
	5,000	44	7	5.99	+ 16*	18

* Presence of the filter aid apparently interfered with electrophoretic mobility measurements, and values may be anomalous.

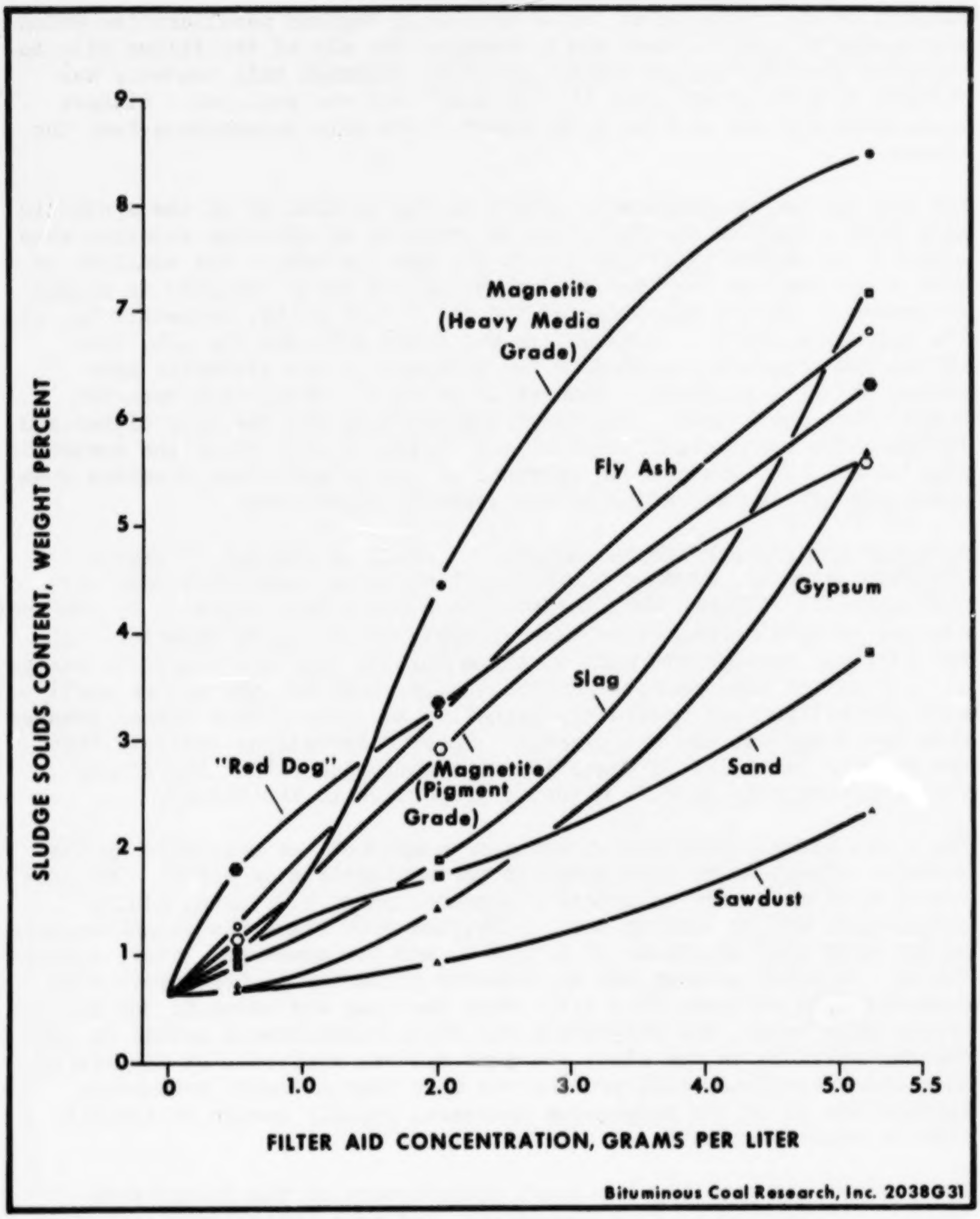


Figure 15. Effects of Filter Aids Alone on Solids Content of Synthetic Coal Mine Drainage Sludge

Several of the filter aids tested exhibited various peculiarities which are worthy of note. There was a tendency for all of the filter aids to separate from the sludge during settling, although this tendency was reduced to some extent when the coagulant aid was employed. Sludges containing fly ash or slag were judged to be more homogeneous than the others.

The fly ash had no measurable effect on the initial pH of the synthetic mine water, despite the fact that it produced an alkaline solution when added to deionized water (pH 9.4 at 500 ppm fly ash). The addition of either the sand or the "red dog" to deionized water resulted in slight increases in pH (on the order of 1.0 and 0.5 pH units, respectively, at the 5,000 ppm level). However, as was found with the fly ash, this effect was apparently masked in the presence of the synthetic mine water, and only negligible changes in pH (≤ 0.1 unit) were observed under these conditions. The blast furnace slag was the only filter aid tested which had a significant effect on the initial pH of the synthetic mine water. For example, an increase of 2.6 pH units was observed when 5,000 ppm of slag was added to the synthetic mine water.

Although the fly ash sample contained a small percentage of ferromagnetic material, sludges containing the fly ash exhibited only very weak magnetic response when tested with a small hand magnet. By contrast, sludges containing magnetite were strongly magnetic, as expected. It was possible to separate much of the magnetite from the sludge by manipulation of the hand magnet. Interestingly, however, the sludge particles themselves were moderately magnetic, and this effect seemed greater when the coagulant aid was present. These observations indicate that the smaller particles of magnetite were entrapped within the sludge flocs, giving rise to bulk magnetic properties in the sludge.

The blast furnace slag had an alkaline component, as evidenced by its definite effect on pH when added to the synthetic mine water. The lime requirement necessary to attain a terminal pH of 7.8 during sludge preparation was reduced to 0.78, 0.74, and 0.60 times the stoichiometric amount with slag additions of 0.5, 2.0, and 5.0 grams per liter, respectively. A minor problem was encountered primarily at the lowest slag concentration employed (0.5 g/l); when the slag was added to the synthetic mine water, the suspension was still sufficiently acidic to decompose sulfides in the slag, and some H_2S was evolved. At the higher slag concentrations, this problem was much less evident, presumably because the pH of the suspension increased rapidly enough to inhibit sulfide decomposition.

The sawdust was probably the least satisfactory of the filter aids tested. It behaved as a pH depressant, and some irregularities were noted in the changes of the suspension pH with time after sawdust addition. This may have been due to the presence of resinous materials leached from the wood, which was indicated by a considerable amount of foaming at the liquid surface during aeration. A portion of the sawdust also tended to float in the container, rather than settling with the sludge.

The usefulness of pigment grade magnetite in this application must be discounted since, in addition to its relatively high cost ($0.17 per pound), problems were encountered in handling the material. With a consistency much like that of carbon black, it tended to coat all surfaces with which it came in contact. It also tended to foul the pores of the air sparger, and considerable difficulty in subsequent cleaning of the apparatus was experienced.

Filtration Tests

In the first series of filtration tests, each of the filter aids was employed at a concentration of 2,000 ppm (2.0 g/l) in the synthetic coal mine water sludge suspension. The results of these tests are summarized in Table 20. The data represent averaged values from duplicate experiments. The filter aids are listed in order corresponding to increasing cake moisture of the filtered solids. It should be noted that this ranking also corresponds to the filtration rate in terms of pounds of dry solids/sq ft/hr. Thus, on the basis of cake yield and moisture content, the more effective filter aids are at the top of the list.

The data for filtrate yields in Table 20 do not appear to conform to the trends shown by the other results. It should be pointed out, however, that of all the experimental measurements, the values for filtrate yields were the least reproducible. Differences on the order of 10 ml in filtrate volumes from duplicate experiments were not uncommon, and this difference corresponds to 1.3 gal/sq ft/hr. Consequently, with the possible exception of the result from the test with "red dog," it is felt that there are essentially no significant differences among the values for filtrate yields. In all of these tests, the filtrates appeared to be quite clear and free of suspended solids.

Recent results reported by investigators of the Johns-Manville Corporation afford an interesting comparison with the data from the present study. These workers observed filtration rates on the order of 30 gal/sq ft/hr and cake solids contents of between 25 and 45 percent during precoat filtration tests with diatomaceous earth (Celite 501) at one field site, where various combinations of lime, limestone, and magnesite were used to treat the coal mine discharge.(14) Filtered sludges obtained by lime-limestone or lime-magnesite treatment had noticeably lower solids contents (29.6 and 24.8 percent, respectively) than did those obtained by treatment with the limestone-magnesite combinations. These values compare favorably with those obtained using some of the filter aids in the present study, where the sludges were produced by lime treatment alone. On the other hand, our measured filtration rates are considerably lower than those reported by the Johns-Manville workers. It should be recognized, however, that there were significant differences in both the methods and materials employed in these two studies, and comparisons among the results may not be entirely appropriate.

TABLE 20. EFFECTS OF VARIOUS FILTER AIDS ON THE FILTRATION PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

Filter Aid*	Filter Cake Properties		Filtration Rate	
	Moisture, Percent	Solids, Percent	lb dry solids/sq ft/hr	gal filtrate/sq ft/hr
Magnetite (pigment grade)	61.7	38.3	0.265	19.8
Fly ash	70.7	29.3	0.201	21.7
"Red Dog"	73.1	26.9	0.146	26.2
Sand	76.8	23.2	0.112	20.0
Slag	78.4	21.6	0.105	22.5
Magnetite (heavy media grade)	81.3	18.7	0.092	20.7
Sawdust	85.9	14.1	0.060	23.1
Gypsum	86.5	13.5	0.053	23.7
Control†	87.3	12.7	0.053	21.2

* Filter aid concentration was 2,000 ppm (2.0 g/l) in all tests.

† Raw sludge only; no filter aid added.

In the second series of filtration tests, two of the filter aids were employed in successively increasing amounts to determine the effect of filter aid concentration on dewatered sludge properties. The filter aids chosen were blast furnace slag, based on its performance as indicated by Figure 15, and "red dog," which performed well in the preliminary filtration tests (Table 20). The results of these tests are shown in Table 21 and Figure 16. All data represent averaged values from duplicate determinations. The data show an apparent increase in filter cake solids contents with increasing filter aid concentration, and the results with the "red dog" are slightly better than those with the slag. With regard to filtration rates, a similar trend is indicated by the data for filter cake yields, although the differences between the two filter aids are not as pronounced. In fact, in view of the variations in cake yields shown by Figure 16, it would appear that there are no substantial differences between the effects of the two filter aids at each concentration level up to and including 5.0 g/l. The sudden divergence of the curves at 6.0 g/l is unexpected, and indicates that either one or both of the values at this concentration may be anomalous.

The data for filtrate yields show slight (although probably negligible) increases in the volume of filtrate with increasing filter aid concentration. As indicated by Figure 16, this increase was rather regular when slag was employed, but the results for "red dog" were erratic. In fact, there is actually a tendency toward decreased filtrate volumes at the higher "red dog" concentrations, and this situation might be expected in view of the greater cake accumulations (reflected by cake yield data) at the higher concentrations of filter aid.

In summary, it is felt that the results of these filtration tests have failed to show any dramatic improvements in sludge dewaterability through the use of filter aids in the manner described (i.e., in a "body feed" rather than as precoat materials). However, the slight improvements which were observed may be sufficient to justify the use of some of the cheaper, more readily available materials for this application, especially in cases where such materials may be considered marginally useful waste products themselves.

Seeding Experiments

The results of experiments on seed crystal size are presented in Table 22. Compared with the results for the control test where no seed material was present, the data show that measurable increases in sludge settling rate and decreases in settled sludge volume were effected by the presence of the seed material. However, the similarities among the results for the three particle size fractions indicate that there were no significantly different effects on sludge properties due to seed crystal size. In this regard, it should be noted that microscopic examination of the sieved material revealed that all size fractions actually consisted of spherical agglomerates of even smaller sized particles. Consequently, it is quite possible that many of these agglomerates were

TABLE 21. EFFECTS OF FILTER AID CONCENTRATION ON THE FILTRATION PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

Filter Aid	Filter Aid Concentration, g/l	Filter Cake Properties		Filtration Rate	
		Moisture, Percent	Solids, Percent	lb dry solids/sq ft/hr	gal filtrate/sq ft/hr
Control*	---	87.3	12.7	0.053	21.2
Slag	0.5	84.8	15.2	0.078	20.2
	2.0	78.4	21.6	0.105	22.5
	3.0	74.8	25.2	0.155	22.4
	4.0	71.5	28.5	0.172	23.3
	5.0	66.7	33.3	0.217	22.9
	6.0	63.5	36.5	0.277	25.4
"Red Dog"	0.5	81.8	18.2	0.064	25.8
	2.0	73.1	26.9	0.146	26.2
	3.0	67.4	32.6	0.162	27.2
	4.0	62.6	37.4	0.169	22.3
	5.0	60.3	39.7	0.225	21.8
	6.0	56.4	43.6	0.211	23.5

* Raw sludge only; no filter aid added.

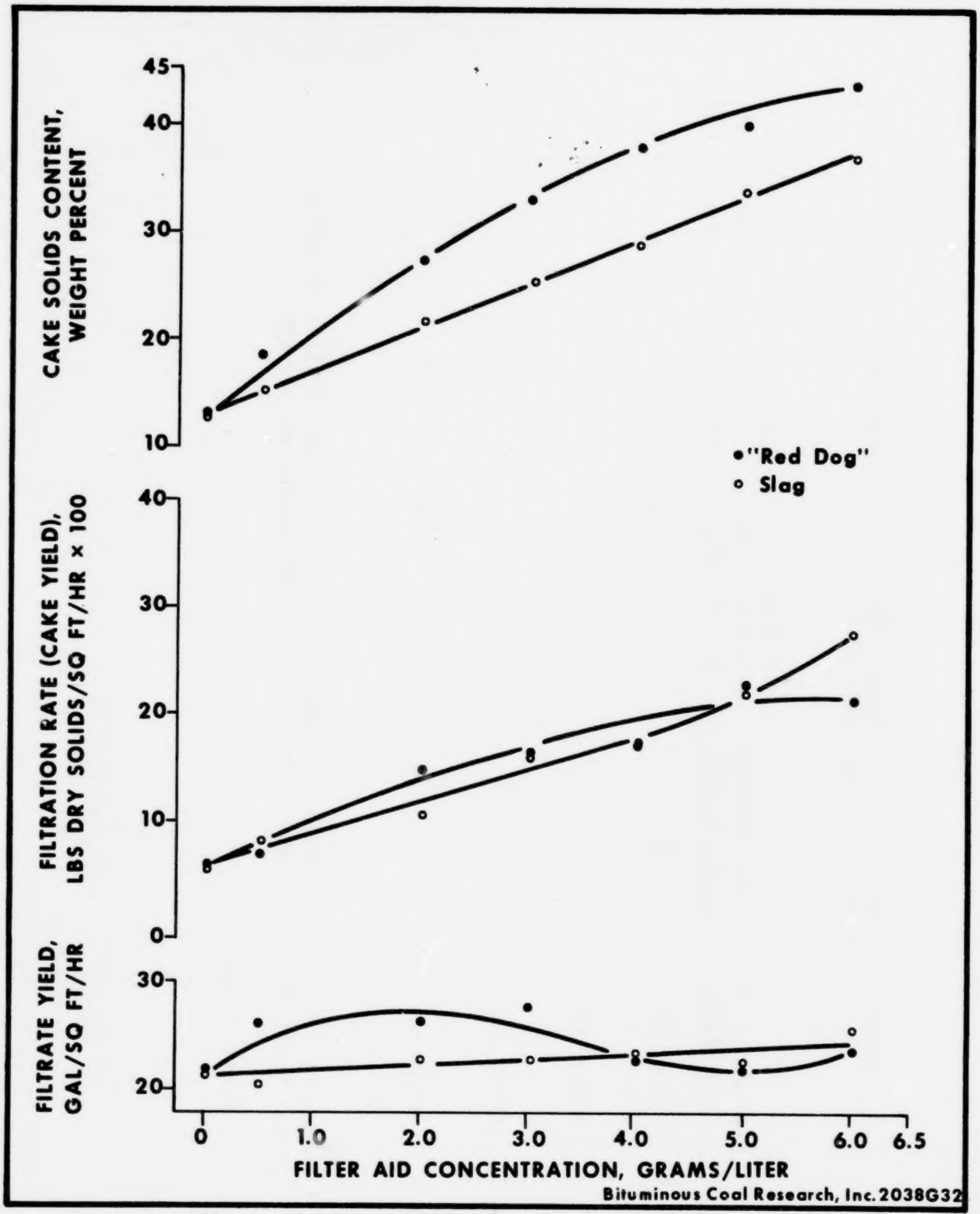


Figure 16. Effects of Filter Aid Concentration on Filtration Properties of Synthetic Coal Mine Water Sludge

TABLE 22. SYNTHETIC COAL MINE WATER SEEDING EXPERIMENTS - EFFECT OF SEED CRYSTAL SIZE*

Test No.	Seed Material Mesh Size+	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
418-38	50 x 80	86	125	0.89	14
418-40	100 x 140	87	130	0.57	14
418-42	200 x 325	87	125	0.63	12
418-44	Control	80	145	0.57	12

* Anhydrous ferric oxide used as a seed material at a concentration of 100 ppm in all tests except control. Stirring rate maintained at 300 rpm.

+ U.S. Sieve Series

broken down by attrition during sludge preparation, even though care was taken to minimize agitation of the suspension. The apparent absence of a particle size effect must therefore be considered as a conditional result subject to further experimentation.

The results of tests on seed crystal amount are shown in Table 23. The data reveal a definite increase in sludge settling rate and solids content and a decrease in sludge volume with increasing amounts of seed material added. Offsetting these improvements, however, is the fact that residual turbidity increased significantly as the amount of seed material was increased. This observation suggests that a considerable portion of the relatively finely divided seed material remained in suspension, i.e., the seed particles had failed to function as precipitation nuclei for the growth of larger, heavier sludge flocs. This likelihood is further supported by the fact that very similar overall results were obtained in the series of tests with filter aids; comparison of the results in Table 18 at filter aid concentrations of 500 and 2,000 ppm, for example, shows that in most cases sludge volumes and solids contents were of the same order of magnitude as those measured using ferric oxide as a seeding material. (The differences in sludge volumes by a factor of about 10 is explained by the fact that in the filter aid studies, settling tests were conducted on 100-ml portions of the sludge suspensions, whereas in the seeding tests the entire sample was transferred to a 1,000-ml graduated cylinder. This same consideration probably also explains the lack of agreement between measured settling rates in the two series of tests.) Thus, it is concluded that the relatively dense (about 5.1 g/ml) ferric oxide behaved more as a sludge "builder," similar to the filter aids previously employed, than as a seed material providing precipitation nuclei. The situation is admittedly ambiguous, and interpretation of the results is complicated by the fact that the filter aids were also introduced prior to lime addition, and could therefore have provided nucleation sites during sludge precipitation However, it is generally recognized that the addition of a strong alkali to a solution containing iron results in the extremely rapid precipitation of a disordered (ferrous hydroxide) or amorphous (hydrous ferric oxide) precipitate, and it seems unlikely that seeding materials would be beneficial under such conditions. Seed crystals are ordinarily employed to provide sites for the growth of ordered crystalline phases, often from pure solutions, in which conditions of temperature, pressure, degree of supersaturation, and other critical factors are carefully controlled.

The results of experiments on the effect of stirring rate are shown in Table 24, and the data indicate that within the rather narrow range of stirring speeds employed, no significant changes in sludge properties were apparent. The tendency towards slight increases in solids contents (seeded tests) and decreases in sludge volumes (seeded and control tests) with increasing stirrer speed may have been due to the production of smaller particles at the higher stirring rates and, subsequently, their more efficient packing in the settled sludge. The relative differences in the results are not large, however, and may be within the

TABLE 23. SYNTHETIC COAL MINE WATER SEEDING EXPERIMENTS - EFFECT OF SEED CRYSTAL AMOUNT*

Test No.	Concentration of Seed Material, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
418-44	0 (Control)	80	145	0.57	12
418-42	100	87	125	0.63	12
418-55	200	101	110	0.79	17
418-53	500	103	100	1.03	22
418-51	1,000	118	85	1.71	36
418-49	2,000	141	75	3.10	59

* 200 x 325 mesh anhydrous ferric oxide used as a seed material in all tests except control. Stirring rate maintained at 300 rpm.

TABLE 24. SYNTHETIC COAL MINE WATER SEEDING EXPERIMENTS - EFFECT OF STIRRING RATE*

Test No.	Stirring Rate, rpm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
418-49	300	141	75	3.10	59
418-57	360	123	70	3.40	78
418-59	420	150	70	3.46	84
418-61	480	121	65	3.86	90
Control	300	80	145	0.57	12
Control	360	91	125	0.46	12
Control	480	96	125	0.54	13

* 200 x 325 mesh anhydrous ferric oxide (2,000 ppm) used as a seed material in all tests except control tests.

limits of experimental error. Nevertheless, one result which is believed to be significant is the marked increase in turbidity of the seeded samples with increasing stirrer speeds. This is believed to be related to increasing breakdown of the initially agglomerated seed particles, as discussed earlier, especially since no similar effect was noted during the control (unseeded) tests. These findings suggest that at least in this instance, the most efficient use of the sludge additive (seeding material) will involve some optimum stirring rate which is great enough to maintain the material in suspension during sludge precipitation, yet not so great as to degrade the material by attrition during mixing. This same statement might also apply in the case of other sludge additives (e.g. certain of the filter aids tested earlier), and should be considered in any future tests of this nature.

The results of tests using dried sludge samples as seeding materials are shown in Table 25. In general, the data fail to show any appreciable differences between the effects of the ordinary sludge and the freeze-dewatered sludge at a given concentration level. Furthermore, a comparison of these data with the data from tests using anhydrous ferric oxide (shown in Table 23) reveals that, with few exceptions, the overall results are quite similar for each seed material at each concentration level. The main discrepancies appear at the 1,000 ppm level, where the data indicate that a greater sludge density was obtained using the ferric oxide. On the other hand, the use of ferric oxide as the seed also resulted in a higher supernatant liquid turbidity after the 30-minute settling period.

From a comparison of the results from the seeded and unseeded (control) tests shown in Table 25, it is apparent that at least small increases in sludge density can be effected by adding a portion of previously obtained sludge to the system before lime neutralization. This observation may in fact be the most significant finding based on the results summarized in Table 25, and is quite likely a major factor in the reasoning which has led to various coal mine drainage treatment schemes involving sludge recirculation.

Sludge Heating and Freezing

Heating Experiments

The results of the first series of experiments on heating the mine water before lime addition are summarized in Table 26. The data show that increasing temperature resulted in reduced sludge volumes and increased sludge solids contents, i.e., an overall increase in sludge density was effected. On the other hand, the sludge settling rate was apparently unaffected by temperature, and the trend to higher turbidity values indicates a tendency toward dispersion or peptization of the sludge with increasing temperature. These observations, and the fact that the overall increases in sludge density were relatively small, suggest that preheating the mine water before lime addition is not a

TABLE 25. RESULTS OF SYNTHETIC COAL MINE WATER SEEDING EXPERIMENTS WITH DRIED SLUDGE SAMPLES*

Test No.	Seed Material	Concentration of Seed Material, ppm	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
418-44	None (Control)	--	80	145	0.57	12
418-69	Air-dried sludge	100	96	120	0.59	12
418-71	Air-dried sludge after freeze-dewatering	100	106	125	0.71	14
418-68	Air-dried sludge	1,000	157	115	1.36	16
418-70	Air-dried sludge after freeze-dewatering	1,000	110	115	1.34	26

* Minus 325 mesh sieve fraction of seed material used in all seeding tests; stirring rate was maintained at 300 rpm in all tests including control.

TABLE 26. EFFECT OF HEATING MINE WATER BEFORE LIME ADDITION ON BEHAVIOR AND PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

Test No.	Temperature, C	Sludge Settling Rate, ml/min*	30-Minute Settled Sludge Volume, ml*	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
418-3	22 (room)	101	130	0.56	9
418-5	40	126	100	0.64	14
418-7	60	100	105	0.60	26
418-9	80	107	75	0.90	24

* Measured in a 1,000-ml graduated cylinder after sludge had cooled to room temperature.

feasible approach to sludge densification. Furthermore, such an approach would almost certainly be impractical from the standpoint of cost.

The results of the second series of tests, involving direct heating of the concentrated (gravity-settled) sludge, are shown in Table 27. Again, the results are not encouraging, and the data indicate that no really significant changes in sludge volumes, solids contents, or settling rates were effected by heating and subsequent cooling of the concentrated sludge. (The extremely low settling rates indicated are due to the fact that, because of preliminary sludge concentration and separation, the sludge was already in the compression zone of settling after being transferred to the 100-ml graduated cylinder.)

Portions of all sludges obtained during the first two series of heating tests were dried and subjected to x-ray diffraction analysis. It was anticipated that the sludges might become dehydrated during heating, resulting in the formation of more crystalline iron oxide species. However, the only iron compound identified was evidently α-FeOOH (synthetic goethite), and this compound was present in all samples including those prepared at room temperature. The diffraction pattern lines for the samples from Tests 418-7 and 418-9 at 60 and 80 C, respectively; see Table 26) seemed to be slightly stronger and more intense than those for other samples, indicating that at least some improvement in crystal ordering was induced at the higher temperatures. In addition, it was observed that the color of the sludge prepared at 80 C (Test 418-9) was darker than those prepared at the other temperatures.

In the third series of tests, sludge concentrates were heated as in the second series, but settling rates and sludge properties were measured before the sludge suspensions were allowed to cool, and measurements were repeated after the sludge samples had cooled to room temperature and were resuspended. The results of these tests are presented in Table 28. The data show slight although measurable increases in solids contents and more appreciable decreases in settled sludge volumes for sludges allowed to settle immediately after heating. Under these conditions, therefore, it is evident that sludge density can be increased by heating alone. On the other hand, when the sludges were resuspended after first being allowed to cool to room temperature, settled sludge volumes and solids contents reverted to approximately the same values as were found for the control test at room temperature (Table 27). Consequently, it is apparent that sludge dehydration (or densification) by heating is a reversible process, at least within the temperature range employed in these studies (22 to 80 C) and this behavior would seem to militate against the feasibility of direct heating as a means of sludge densification.

It should be noted that the technique of sludge densification by heat treatment has been applied successfully to the dewatering of sewage sludges. A process, known as the Porteous Process, was developed in

TABLE 27. EFFECT OF HEATING ON BEHAVIOR AND PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

Test No.	Temperature, C	Sludge Settling Rate, ml/min*	30-Minute Settled Sludge Volume, ml*	Sludge Solids Content, Weight Percent
415-90	22 (room)	0.06	98.0	0.50
415-94	40	0.13	96.0	0.52
415-86	60	0.12	96.5	0.54
415-88	80	0.08	97.5	0.67

* Measured in a 100-ml graduated cylinder after sludge had cooled to room temperature.

TABLE 28. EFFECT OF HEATING AND SUBSEQUENT COOLING ON BEHAVIOR AND PROPERTIES OF SYNTHETIC COAL MINE WATER SLUDGE

		Heated Sludge			Resuspended Sludge After Cooling to Room Temperature		
Test No.	Temperature, C	Settling Rate, ml/min*	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Settling Rate, ml/min*	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent
418-32	40	0.25	91.5	0.51	0.18	94.5	0.46
418-30	60	1.60	78.0	0.66	0.27	92.0	0.45
418-34	80	3.60	66.0	0.73	0.12	96.5	0.50

* Measured in a 100-ml graduated cylinder.

England and has been marketed in the United States since 1968 by BSP Corporation, San Francisco, California.(15 through 17) The process has been adopted by several major European cities but has found only limited acceptance so far in this country. The major step in the process involves steam-heating of the sewage sludge at temperatures of 350 to 390 F (177 to 199 C) and pressures of 180 to 210 psi (12.2 to 14.3 atm), and it will be noted that these conditions are considerably different from those employed in the present studies. The costs of the Porteous Process in this country have been reported at between $1.50 and $3.50 per ton of dry solids, and part of the overall cost may be offset by recovering the calorific value of the filtered sludge. Although filter cakes from the process reportedly contain as high as 60 percent solids, it is doubtful whether this rather sophisticated approach could be adapted economically for dewatering of coal mine drainage sludge. This conclusion is supported by the fact that work done elsewhere on the pressure-heat treatment of mine drainage sludges led to discouraging results.(18)

Freezing Experiments

The technique of freeze-dewatering has been investigated by several workers for the treatment of sewage sludges.(19 through 26) Moreover, this approach has been incorporated at several full-scale sewage treatment plants in England and sludge volumes processed are on the order of 4,800 gallons per day at one location.(22,23) The overall costs (capital and operating) of the sludge freezing process reportedly ranged between $1.47 and $0.35 per thousand gallons of water treated, depending to a large extent on the solids content of the thickened sludge subjected to freezing.(23) Sludge freezing costs were minimized by recycling the refrigerant (ammonia) through the sludge thawing tanks; in this way, heat acquired by the refrigerant during the freezing step was liberated during the thawing step. Once a particular batch of sludge had been frozen, the refrigerant flow was simply reversed. The resulting sludge could be easily dewatered to 60 to 70 percent solids by gravity draining.

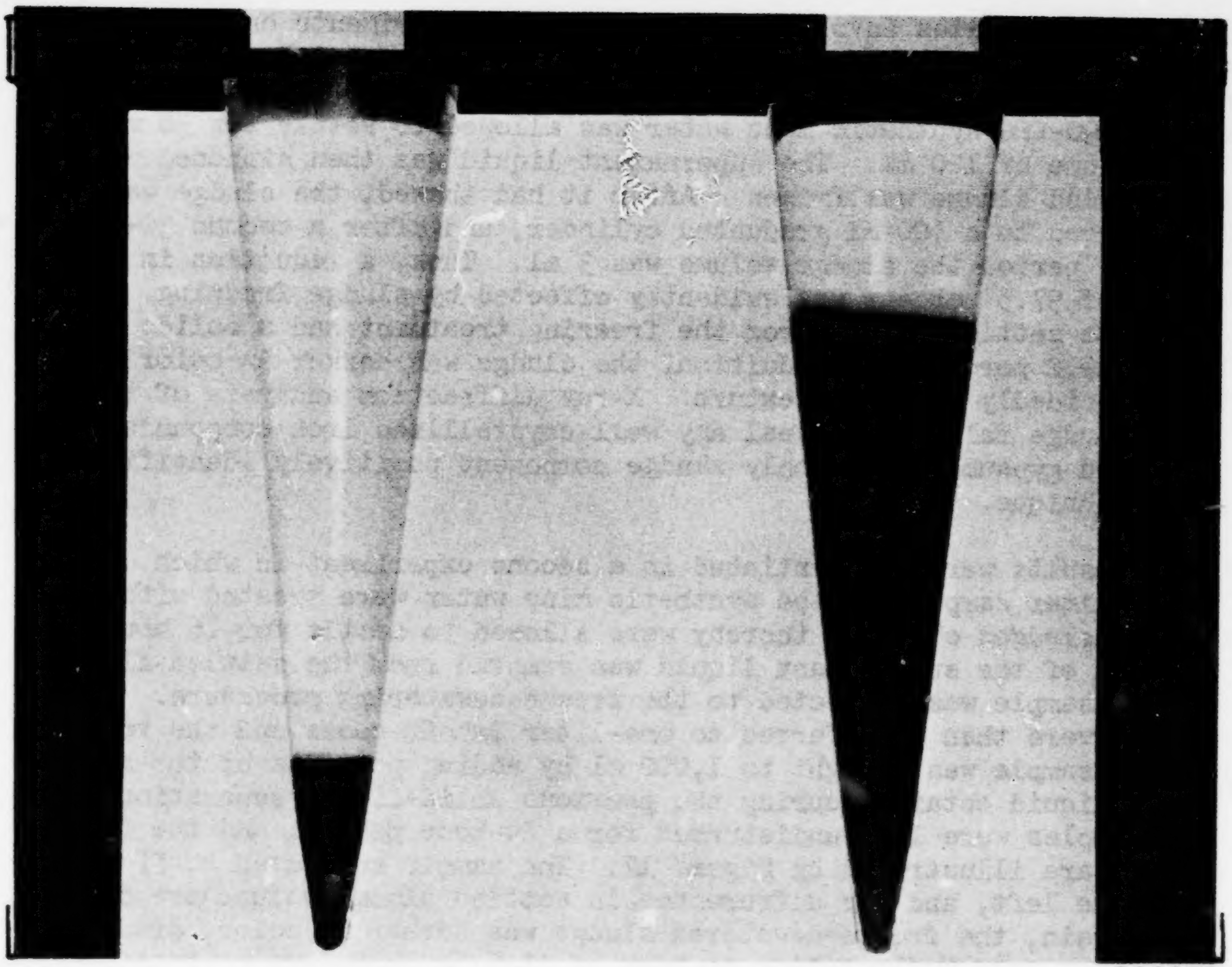
One limitation of the sludge freezing technique, mentioned by several investigators, is that the sludge must be frozen at a relatively slow rate.(23,24) This is so because water is in effect "squeezed" out of the gelatinous sludge flocs as formation of the solid state is approached. Rapid or "flash" freezing of the sludge is undesirable since physically entrapped water is retained within the sludge flocs, resulting in little or no dewatering after thawing. It should be noted, however, that the results of a study reported very recently indicate that substantially higher sludge freezing rates may be feasible through the use of a film-freezing technique.(25) Sludge freezing rates of about 4.2 ml/min were successfully achieved, whereas earlier studies had indicated that practical freezing rates were on the order of 0.40 ml/min.(24)

The present studies involved two preliminary experiments on the effects of freezing a synthetic coal mine drainage sludge. In the first experiment, the sludge prepared by lime treatment of a 1,000-ml batch sample of the WQO-EPA synthetic mine water was allowed to settle for 30 minutes to a volume of 120 ml. The supernatant liquid was then siphoned off and the settled sludge was frozen. After it had thawed, the sludge was transferred to a 100-ml graduated cylinder, and after a second 30-minute settling period the sludge volume was 3 ml. Thus, a reduction in sludge volume of 97.5 percent was evidently effected by sludge freezing. The 30-minute settled sludge from the freezing treatment had a solids content of 9.2 percent. In addition, the sludge was darker in color and had a decidedly granular texture. X-ray diffraction analysis of the dried sludge failed to reveal any well-crystallized iron compounds, however, and gypsum was the only sludge component positively identified by this technique.

These results were substantiated in a second experiment in which duplicate 4-liter samples of the synthetic mine water were treated with lime and the sludges obtained thereby were allowed to settle for 16 hours. The bulk of the supernatant liquid was removed from the settled sludges and one sample was subjected to the freeze-dewatering procedure. The sludges were then transferred to one-liter Imhoff cones and the volume of each sample was brought to 1,000 ml by adding portions of the supernatant liquid obtained during the previous solid-liquid separation step. Both samples were left undisturbed for a 24-hour period, and the final results are illustrated by Figure 17. The sample subjected to freezing is on the left, and the differences in settled sludge volume are obvious. Again, the freeze-dewatered sludge was darker in color, granular in texture, and had a solids content of 11.6 percent. By contrast, the solids content of the control sludge sample (on the right in Figure 17) was only 0.90 percent after the 24-hour settling period.

The preliminary experiments were followed by additional tests using the actual mine waters listed in Table 1. The purposes of these tests were to determine whether comparable results could be achieved with actual mine water sludges, and to investigate the effect of dissolved aluminum during the process. With regard to the latter, it has been reported that the presence of at least 20 ppm of aluminum (presumably present in the sludge as coprecipitated aluminum hydroxide) is essential for efficient dewatering during (sewage) sludge freezing.(25) Since at least a few actual mine waters (e.g., Keystone and Brinkerton) contain essentially no measurable aluminum, this apparent constraint regarding aluminum content could be significant factor in the conditioning of mine drainage sludges by freeze-dewatering.

The results of these sludge freezing experiments are summarized in Table 29. Sludges were prepared in the usual manner (addition of hydrated lime to a final pH of 7.8) and aluminum (as $Al_2(SO_4)_3 \cdot 18H_2O$), when added, was dissolved in the 1,000-ml mine water sample before lime neutralization.



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Sludge Volume after Freeze-dewatering

Sludge Volume before Freeze-dewatering

Figure 17. Effect of Freeze-dewatering on Volume of Synthetic Coal Mine Drainage Sludge

TABLE 29. RESULTS OF FREEZE-DEWATERING EXPERIMENTS WITH ACTUAL COAL MINE WATERS

Test No.	Mine Water	Al^{3+} Added, ppm	30-Minute Settled Sludge Volume Before Freezing, ml	30-Minute Settled Sludge Volume After Freezing, ml	Reduction in Sludge Volume, Percent	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
421-5C	Keystone	None	70	--	--	1.14	62
421-6	Keystone	None	65	11	83.1	5.17	40*
421-6A	Keystone	20	95	14	85.3	4.50	32*
421-7	Keystone	100	225	20	91.1	5.10	42*
421-45	S. Greensburg	None	40	--	--	0.51	44
421-46	S. Greensburg	None	40	4	90.0	3.97	12*
421-46A	S. Greensburg	20	70	5	92.9	4.53	18*
421-25C	Brinkerton	None	45	--	--	0.53	45
421-26	Brinkerton	None	50	5	90.0	4.29	25*
421-26A	Brinkerton	20	70	7	90.0	4.57	21*
421-27	Brinkerton	100	210	12	94.3	5.13	18*
421-35C	Tarrs	None	100	--	--	0.52	33
421-36	Tarrs	None	100	6	94.0	4.84	14*
421-36A	Tarrs	20	130	7	94.6	5.14	12*

* After settling of freeze-dewatered sludge.

The data in Table 29 show that, as with the tests involving the synthetic mine water, significant reductions in settled sludge volume (on the order of 90 percent) were effected by sludge freezing. In addition, decreases in turbidity were noted as a result of the freeze-dewatering process. Solids contents of the 30-minute settled sludges after freezing were on the order of 4 to 5 percent. Although these solids content values are somewhat lower than those observed for the synthetic mine water sludges after freeze-dewatering, it is felt that they still represent substantial increases compared with the corresponding values for the unfrozen (control) sludges.

Concerning the effect of added aluminum on sludge properties, there is a trend toward slightly greater sludge volume reductions and increased solids contents in the sludge after freezing as the amount of aluminum increases in the system. However, it should be noted that the addition of aluminum also has a pronounced effect on the original volume of the settled sludge before freezing For example, the addition of 20 ppm of Al^{3+} to each of the four mine waters led to increases in initial sludge volumes of from 30 to 75 percent. In view of these findings, therefore, there seems to be no justification for the intentional addition of aluminum salts as a means of controlling mine drainage sludge properties during the freeze-dewatering process.

In summary, the data in Table 29 show surprisingly good agreement among the results for each of the four mine waters tested. It would appear that the technique of freeze-dewatering holds considerable promise as a potential method of coal mine drainage sludge densification. Results of these tests, as well as those referred to earlier involving sewage sludge treatment, suggest that freeze-dewatering is a relatively simple operation which could be applied to any type of sludge resulting from various coal mine drainage treatment processes. From this standpoint, therefore, freeze-dewatering might find wider acceptance than other potential sludge densification processes (e.g., magnetic sludge preparation) which are conceptually more complex or are limited to certain types of coal mine discharges. The technology of freeze-dewatering seems to be rather well developed, and the only major obstacle to this approach apparently involves the question of economic feasibility. In view of the fact that this is one of the most successful methods of sludge conditioning (and possibly the simplest) explored during this program, it is felt that further work on this technique would be appropriate.

Miscellaneous Approaches - Coprecipitation of Calcium Carbonate

As described earlier, it was observed that magnetic sludges obtained from certain of the carbonated mine waters tested, e.g., Keystone and Brinkerton, contained calcium carbonate. These sludges generally occupied smaller volumes after settling and had higher solids contents than did similar sludges prepared from mine waters essentially free of dissolved CO_2, e.g., synthetic mine waters containing comparable iron concentrations. In addition, it is known from work at BCR and elsewhere that limestone treatment of a given mine water usually results in a denser sludge than that obtained by hydrated lime treatment. It was reasoned, therefore, that the intentional addition of CO_2 to mine water prior to lime neutralization might have a pronounced effect on the properties of the resulting sludge.

This was verified during one preliminary experiment where a synthetic mine water was sparged with CO_2 for 15 minutes before lime was added (as a slurry) to a final pH of 7.8. The resulting sludge settled to a volume of 20 ml in 30 minutes and had a solids content of 8.9 percent by weight. In contrast, a control sludge obtained by the usual lime neutralization procedure without prior CO_2 sparging settled to only 180 ml and had a solids content of 0.4 percent.

Because lime is consumed in reacting with CO_2 to form coprecipitated calcium carbonate,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

it is obvious that the presence of dissolved CO_2 will increase the lime requirement during treatment. This aspect was investigated in a series of experiments in which lime was employed (as a slurry) in multiples of the stoichiometric requirement based on the hot acidity[5] of the synthetic mine water (931 ppm). In all the experiments involving CO_2 addition, a 15-minute CO_2 sparging period was employed previous to lime addition and the 30-minute reaction period. Control experiments (no prior CO_2 sparging period) were also conducted for comparison.

The results of these experiments are summarized in Table 30. The data show that significant reductions in sludge volume, on the order of 90 percent in all cases, were achieved as a result of calcium carbonate coprecipitation. (The presence of $CaCO_3$ in the sludges from CO_2-addition tests was confirmed through x-ray diffraction analysis.) Interestingly, settled sludge volumes were essentially the same for all the CO_2-addition tests despite the fact that solids contents of the sludges increased regularly with increasing amounts of lime utilized. Counteracting the apparent beneficial effects of CO_2 addition is the fact that turbidities in these samples were unusually high compared to the control samples. This tendency toward increased turbidity has also been noted in past BCR studies on limestone treatment of coal mine drainage. In fact, the sludges obtained from the CO_2-addition tests bore a striking resemblance to those obtained from limestone neutralization experiments in terms of color and texture, in addition to settling behavior.

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[5] The term "hot acidity" refers to the mine water acidity, as ppm calcium carbonate equivalents, determined by the usual titration procedure involving heating of the sample to remove CO_2 content. Conversely, the "cold acidity" is determined with no prior heating of the sample, and consequently dissolved CO_2, when present, is also titrated, leading to higher values.

TABLE 30. EFFECT OF CO_2 ADDITION ON LIME REQUIREMENT AND SLUDGE PROPERTIES DURING LIME TREATMENT OF SYNTHETIC COAL MINE WATER

	Test No.	Amount of $Ca(OH)_2$*	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU	Final pH After Lime Treatment†	Reduction in Sludge Volume, Percent
Control Tests	418-86C	1.00 X	107	120	0.57	11	5.78	--
	421-8C	1.10 X	118	145	0.49	11	7.82	--
	418-96C	1.25 X	83	160	0.64	10	9.02	--
	418-94C	1.50 X	48	190	0.59	9	11.08	--
	418-90C	2.00 X	64	180	0.79	9	12.00	--
	418-92C	3.00 X	60	330**	0.75	7	12.31	--
CO_2 Tests	418-86	1.00 X	‡	15	1.90	74	6.02	87.5
	421-8	1.10 X	‡	20	1.95	81	7.70	86.2
	418-96	1.25 X	‡	20	2.42	58	8.15	87.5
	418-94	1.50 X	‡	15	2.86	71	8.15	92.1
	418-90	2.00 X	‡	20	4.96	36	8.09	88.9
	418-92	3.00 X	203	35	5.62	28	7.93	89.4

* Multiple of stoichiometric lime requirement based on hot acidity determination.

† pH of suspension after 30-minute lime neutralization/aeration period.

** The sludge was cream-colored; coprecipitated $Mg(OH)_2$ was probably present, accounting for larger sludge volume.

‡ Settling rate could not be measured due to extreme turbidity of the sample.

As indicated by the data in Table 30, noticeable improvements in sludge solids contents were effected by the pretreatment of the samples with CO_2.

With regard to the lime requirement, the data indicate that possibly as much as twice the stoichiometric amount (based on the hot acidity) should be employed in conjunction with CO_2 pretreatment to effect the desired changes in sludge properties. It should be noted that the use of the exact stoichiometric amount (1.00 X) was not sufficient in either case since the terminal pH value was only about 6 after the 30-minute reaction period; furthermore, significant amounts (15 to 25 ppm) of Fe^{2+} remained in solution under these conditions at the end of the reaction period. At all higher lime concentrations employed (1.10 X and above), residual dissolved iron was reduced to the 1 to 2 ppm level.

The presence of relatively large amounts of dissolved CO_2 apparently tends to buffer the system against an overdose of lime, as indicated by the fact that terminal pH values were all close to 8.0 (except for the test at 1.00 X lime) during the CO_2 pretreatment series. By contrast, it may be noted that for the control tests the terminal pH increased appreciably as the amount of lime was increased.

In another series of tests, the lime requirement was based on the cold acidity of the synthetic mine water determined after the CO_2 sparging period, which was varied in duration from 15 to 60 minutes. The results of these tests are summarized in Table 31. These results followed the same general trends as were observed in the earlier tests (Table 30), discussed above. The results of cold acidity determinations shown in Table 31 indicate that only relatively small increases in acidity were effected by increasing the CO_2 sparging period. Since changes in the cold acidity values are presumably an indirect measurement of changes in dissolved CO_2, the data suggest that there is little advantage to be gained by prolonging the CO_2 sparging period beyond 15 minutes. Thus, although increased CO_2 sparging periods may lead to higher solids contents in the sludge as indicated, this gain is offset by increasing lime requirements and overall treatment times.

The effects of calcium carbonate coprecipitation were further substantiated in tests using an actual mine water from the Keystone site. As indicated earlier, this mine discharge appears to have an unusually high dissolved CO_2 content. Three 1,000-ml samples of the mine water were treated, each by a difference approach. With the first sample, nitrogen gas was sparged into the mine water for 15 minutes before lime addition in an attempt to reduce the original dissolved CO_2 concentration. During this period, a portion of the ferrous iron was precipitated as evidenced by the appearance of a blue-green precipitate, and the pH rose from an initial value of 6.3 to 7.5. The cold acidity of the sample was then determined, and 1.00 X lime was added based on this value. The second sample (control) was treated as received using 1.00 X $Ca(OH)_2$ based on the cold acidity value for the raw mine water. The third sample

TABLE 31. EFFECT OF CO_2 SPARGING PERIOD ON LIME REQUIREMENT AND SLUDGE PROPERTIES DURING LIME TREATMENT OF SYNTHETIC COAL MINE WATER

Test No.	CO_2 Sparging Period, minutes	Cold Acidity After CO_2 Sparging Period, ppm $CaCO_3$	Amount of $Ca(OH)_2$ Used, grams/liter	Final pH After Lime Treatment*
421-10C†	None	--	0.7270‡	7.75
421-10	15	2,026	1.4999	7.96
421-18	30	2,061	1.5258	8.09
421-12	60	2,143	1.5865	7.80

Test No.	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU	Reduction in Sludge Volume, Percent**
421-10C†	100	125	0.70	6	--
421-10	140	35	3.61	33	72.0
421-18	157	30	4.37	30	76.0
421-12	140	35	5.11	42	72.0

† Control test; no pretreatment with CO_2.

‡ Amount of lime for control test was 1.05 X stoichiometric requirement based on hot acidity determination; all other amounts were 1.00 X stoichiometric requirement based on cold acidity determination after indicated CO_2 sparging period.

* pH of suspension after 30-minute lime neutralization/aeration period.

** Based on settled sludge volume measured during control test.

was sparged with CO_2 for 15 minutes before lime addition in an effort to determine whether additional dissolved CO_2 could be introduced into the mine water. The lime requirement (1.00 X) was based on a cold acidity determination immediately after the CO_2 sparging period.

Preliminary tests showed that it was not possible to completely oxidize the iron in the nitrogen-purged sample during the usual 30-minute reaction period (presumably due to depletion of dissolved oxygen during the nitrogen purge period). Consequently, the reaction time was increased to two hours for all tests in this series.

The results of these tests are shown in Table 32. The influence of CO_2 content on both the acidity values and sludge properties is apparent from the data. Although the volume of settled sludge from the nitrogen-purged sample was identical to that for the control test, one will note that there is a difference (although small) in the solids contents of the two samples. In addition, the relatively high turbidity in the nitrogen-purged sample reveals that an appreciable amount of sludge was still in suspension, thus in effect decreasing the apparent volume of the settled sludge.

It is clear from these exploratory studies that the effect of dissolved CO_2 is significant, and perhaps has not been given sufficient consideration by other workers involved in mine drainage treatment research. Its importance is particularly noteworthy as pertains to the lime treatment of carbonated or the so-called "alkaline" mine waters (such as Keystone and Brinkerton), although these may be comparatively few in number. Although the presence of dissolved CO_2 as it affects the raw mine water acidity (and therefore, the lime requirement) is probably generally understood, its effect on sludge properties may not have received adequate recognition in earlier studies.

Finally, because of the apparent increases in turbidity caused by the use of CO_2 pretreatment, a brief series of experiments was conducted to ascertain whether the use of coagulant aids could overcome this problem. The anionic polyelectrolyte Genfloc 155 was added at a concentration of 1 ppm to both synthetic mine water control samples and those which had been subjected to a 15-minute CO_2 sparging period. The polyelectrolyte was added during a 1-minute stirring period immediately before settling tests were commenced.

The results of these experiments are shown in Table 33. The data show that significant improvements in clarity of the supernatant liquid were obtained through the use of the coagulant aid. Thus, although CO_2-treated samples were still slightly more turbid than the control samples after the 30-minute settling period, they were considerably less turbid than those prepared in the absence of the coagulant aid (cf. Table 31). Furthermore, although the addition of the coagulant aid resulted in substantial increases in the settling rates (and slight decreases in settled sludge volumes) of the control samples, the relative reductions

TABLE 32. EFFECT OF DISSOLVED CO_2 CONTENT OF SLUDGE PROPERTIES DURING LIME TREATMENT OF A CARBONATED MINE WATER (KEYSTONE)

Test No.	Mine Water Pretreatment	Cold Acidity After Pretreatment, ppm $CaCO_3$	Amount of $Ca(OH)_2$ Used, grams/liter	Final pH After Lime Treatment*
421-37	N_2 - 15 min	234	0.1732	8.35
421-38	None†	549	0.4064	8.45
421-39	CO_2 - 15 min	2,174	1.6095	8.36

Test No.	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU
421-37	110	70	0.88	95
421-38	123	70	1.37	43
421-39	164	35	6.34	48

† Control test.

* pH of suspension after 2-hour lime neutralization/aeration period.

TABLE 33. EFFECT OF CO_2 SPARGING IN CONJUNCTION WITH COAGULANT AID ADDITION ON SLUDGE PROPERTIES DURING LIME TREATMENT OF SYNTHETIC COAL MINE WATER

Test No.††	Mine Water Pretreatment	Amount of $Ca(OH)_2$ Used, grams/liter	Multiple of Stoichiometric Amount	Final pH After Lime Treatment**
421-22C	None	0.7270	1.05 X‡	7.09
421-21	CO_2 - 15 min	1.5739	1.00 X*	8.05
421-24C	None	0.7655	1.10 X‡	7.81
421-24	CO_2 - 15 min	1.7802	1.10 X*	7.95

Test No.	Sludge Settling Rate, ml/min	30-Minute Settled Sludge Volume, ml	Sludge Solids Content, Weight Percent	Turbidity of Supernatant Liquid, JTU	Reduction in Sludge Volume, Percent
421-22C	380	120	0.57	1	--
421-21	†	40	3.34	7	66.7
421-24C	350	120	0.55	1	--
421-24	†	30	4.92	6	75.0

†† 1.0 ppm of Genfloc 155 added in all tests prior to settling period.
** pH of suspension after 30-minute lime neutralization/aeration period.
‡ Based on hot acidity determination.
* Based on cold acidity determination after CO_2 sparging period.
† Sludge flocs settled rapidly without a well-defined solid-liquid boundary.

in sludge volumes and increases in solids contents for the CO_2-treated samples were of the same order of magnitude as those observed earlier in the absence of the coagulant aid.

It should be noted that although this approach involving CO_2 pretreatment may be a novel one as applied to coal mine drainage treatment, it has been tested and patented in conjunction with sewage treatment.(27,28) The procedure involved sparging CO_2 (from incinerator flue gas) into the activated sludge for 10 to 30 minutes, followed by the addition of hydrated lime (27) or hydrated lime plus calcium chloride.(28) With lime alone as the precipitant, the resulting sludge could be vacuum filtered to about 35 percent solids content. With both processes, the filtered sludge was calcined to recover some CaO which could be recycled. In this regard, any extension of this approach to coal mine drainage treatment should involve studies on the use of the residual sludge alkalinity to offset increased lime requirements as a result of preliminary CO_2 addition. Further investigations would be desirable to determine the filtration characteristics (dewaterability) of the sludge, its amenability to CaO and CO_2 recovery by calcination, and the possibility of using the $CaCO_3$ constituent of the sludge with or without additional lime for direct mine water neutralization. Since the $CaCO_3$ is formed via a precipitation reaction, it is presumably in a very finely divided state; because this is a desirable property in the selection of limestones as neutralizing agents for coal mine water,(29) the sludge containing coprecipitated calcium carbonate might compete favorably with pulverized limestones in such an application. On the other hand, it is possible that sludge recycling might negate the original densification effect obtained through the mechanism of $CaCO_3$ coprecipitation. It seems clear that there are several facets of this approach which warrant further investigation.

SECTION VI

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SECTION VII

REFERENCES

1. Bituminous Coal Research, Inc., "Studies on limestone treatment of acid mine drainage," Water Pollution Control Res. Series DAST-33, 14010 EIZ, 01/70, Water Quality Office, Environmental Protection Agency, Washington, D. C. (1970).

2. Kakabadse, G. J. and Whinfrey, P., "The effect of certain ions on the formation of magnetite from aqueous solution," Ind. Chim. Belge 29 (2), 109-12 (1964).

3. Riddoch, J., "The hydrolytic and redox properties of ferric iron, with special reference to the effect of magnesium ions above pH 10," Ph.D. Thesis, Victoria University, Manchester, England, 1964.

4. Kakabadse, G. J., Riddoch, J., and Bunbury, D. St. P., "The effect of magnesia on the formation of magnetite from aqueous solution," J. Chem. Soc. (A), 1967, 576-9 (1967).

5. Stauffer, T. E. and Lovell, H. L., "The oxygenation of iron(II) - relationship to coal mine drainage treatment," Special Research Report SR-69 to the Coal Research Board, Commonwealth of Pennsylvania (Nov. 1, 1968).

6. Pavelic, V. and Saxena, U., "Basics of statistical experiment-design," Chem. Eng. 76 (21), 175-80 (1969).

7. Dorr-Oliver Inc., "Filtration leaf test procedures," Bulletin No. 251 LT, 1955.

8. Matusevich, L. N., "Crystallization in presence of seed crystals," J. Appl. Chem. U.S.S.R. 34, 952-7 (1961).

9. Davies, O. L., ed., "The Design and Analysis of Industrial Experiments," New York: Hafner Publishing Company, 1956. Chapter 7.

10. Aarons, R. and Taylor, R. A., "The DuPont waste pickle liquor process," Proc. 22nd Ind. Waste Conf., Purdue Univ., 1967, pp. 120-5.

11. Anon., "Extent of coal mine drainage pollution, McMahon Creek watershed, Ohio," U.S. Dept. Interior, FWQA Ohio Basin Region, Work Document No. 34, June 1970.

12. Anon., "Sewickley Creek area, Pennsylvania; Monongahela River mine drainage remedial project," U.S. Dept. Interior, FWQA, June 1966.

13. Parsons, W. A., "Chemical Treatment of Sewage and Industrial Wastes," Washington, D. C.: Bulletin No. 215, National Lime Association, 1965. pp. 64-5.

14. Brown, T. S. and Long, B. W., "Neutralization and precoat filtration of concentrated sludge from acid mine water at the Rushton Mining Company in Osceola Mills, Pa. Project CR-82," Johns-Manville Rept. No. E412-8087-S1 to Pennsylvania Coal Res. Board (Nov. 3, 1969). 16 pp.

15. Porteous, I. K., "Mechanical treatment of sewage sludge by the steam-injection method," Municipal Engineering, Dec. 16, 1966. 2 pp.

16. Bulletin No. S114, BSP Corporation, San Francisco, California.

17. Cardinal, P., Jr., "Porteous process," BSP Corporation, San Francisco, California, undated. Unpublished. 12 pp.

18. Glover, H. G., Natl. Coal Board, South Yorkshire Area, England, 1970. Private communication. 2 pp.

19. Clements, G. S., Stephenson, R. J., and Regan, C. J., "Sludge dewatering by freezing with added chemicals," J. Inst. Sewage Purif. 4, 318-37 (1950).

20. Doe, P. W., "The treatment and disposal of wash water sludge," J. Inst. Water Engrs. 12, 409-45 (1958).

21. "The sludge freezing plant at the Stocks reservoir," The Fylde Water Board, J. Brit. Waterworks Ass. 43, 434 and 436 (1961).

22. Doe, P. W., Benn, D., and Bays, L. R., "The disposal of wash water sludge by freezing," J. Inst. Water Engrs. 19, 251-91 (1965).

23. Benn, D. and Doe, P. W., "The disposal of sludge by the freezing and thawing process," Filtr. Separ. 6 (4), 383-9 (1969).

24. Katz, W. and Mason, D. G., "Freezing methods used to condition activated sludge," Water Sewage Works 117, 110-14 (1970).

25. Cheng, C., Updegraff, D. M., and Ross, L. W., "Sludge dewatering by high-rate freezing at small temperature differences," Environ. Sci. Technol. 4 (12), 1145-7 (1970).

26. Farrell, J. B., Smith, J. E., Jr., Dean, R. B., Grossman, E., III, and Grant, O. L., "Natural freezing for dewatering of aluminum hydroxide sludges," J. Am. Water Works Assoc. 62 (12), 787-91 (1970).

27. Davis, N. S. and Foust, O. J. (to North American Rockwell Corp.), "Waste treatment with recycling of flocculating agents," U.S. Pat. 3,440,166 (Apr. 22, 1969). 6 pp.

28. Davis, N. S., Foust, O. J., and Withers, T. W. (to North American Rockwell Corp.), "Waste treatment with recycling of lime," U.S. Pat. 3,440,165 (Apr. 22, 1969). 8 pp.

29. Ford, C. T., "Selection of limestones as neutralizing agents for coal mine water," 3rd Symp. Coal Mine Drainage Res. Preprints, Pittsburgh, Pa., by Coal Ind. Advisory Comm. to Ohio River Valley Water Sanit. Comm., 1970. pp 27-51.

BIBLIOGRAPHIC:

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ACCESSION NO.

KEY WORDS: Coal mine drainage, sludge, sludge conditioning, magnetic sludge, iron removal, sludge densification, sludge disposal, stream pollution, pollution abatement, acid mine water treatment.

ABSTRACT

The purpose of this research was to alleviate present problems in handling and disposal of sludges obtained by lime neutralization of coal mine drainage, through the investigation of various sludge densification techniques. The scope of the work was restricted to bench-scale batch experiments. Tests were largely of an exploratory nature and, as such, did not afford sufficient data to permit detailed cost comparisons among the various techniques.

In the first approach, conditions commonly employed in the lime treatment procedure (lime neutralization and aeration) were altered to produce a dense, fast-settling, ferromagnetic sludge. Although the properties of this sludge are sufficiently unique, the magnetic sludge conversion process includes a requirement for sludge heating and is quite sensitive to the presence of small amounts of aluminum in the original mine water.

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ment procedure involving lime neutralization and aeration. These methods included the use of coagulant aids, sludge bulk additives (filter aids), seeding materials, and sludge heating and freezing.

In addition, exploratory tests were conducted on the introduction of carbon dioxide into the mine water to promote coprecipitation of calcium carbonate during lime addition.

Among the sludge densification methods tested, only three—magnetic sludge preparation, sludge freezing, and CO_2 pretreatment—appeared to be promising in terms of results obtained. Each method led to sludge volume reductions on the order of 90 percent and increases in sludge solids contents of from 0.5 to about 5 percent after 30-minute settling periods. Further developmental work would be desirable to determine the general usefulness and comparative costs of each method as applied to coal mine drainage treatment.

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As a second approach, recognized conditioning methods were applied to coal mine drainage sludges. These methods included the use of coagulant aids, sludge bulk additives (filter aids), seeding materials, and sludge heating and freezing. In addition, tests were conducted on the introduction of carbon dioxide into the mine water to promote coprecipitation of calcium carbonate during lime addition.

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